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CALCIUM SUPERPHOSPHATE AND
COMPOUND FERTILISERS

CALCIUM SUPERPHOSPHATE AND COMPOUND FERTILISERS: THEIR CHEMISTRY AND MANUFACTURE

BY

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PREFACE

TO THE SECOND EDITION

REPEATED requests have been made from many parts of the world, and not least from this country, for a second edition of this book. A portion of the first edition suffered the same fate as many other books—it was lost in the “blitz” on London on 29th December, 1940.

The opportunity to publish a second edition did not occur till 1944, and as requests were essentially for a second edition, and not a new book, it has been decided that the “expressed wish” should be met.

Obviously, after six years, five of these constituting World War No. 2, fertilisers have assumed an importance second only to indigenously-produced food itself. Experiments have been made in intensive cultivation, and in an effort to produce prodigious quantities of food, first for human, and later for animal consumption. These experiments and efforts have met with a large measure of success. The fertiliser industry has not been lacking in enterprise. It has standardised compound fertilisers, thus simplifying production, and it has manufactured large quantities of granular fertilisers, and in some parts of the country it has continued to manufacture uninterruptedly, despite aerial and other such attacks. This contribution to the war effort certainly merits recognition.

Only one new chapter appears in the second edition. This is Chapter I, which attempts to outline in some detail the ramifications of the fertiliser industry, and indicates the changes which are likely to take place in the manufacture of fertilisers in the next few years. There are growing evidences that water-solubility has outlived its usefulness, and that new types of fertiliser are becoming a necessity.

In the other chapters of the book much of the original matter has been preserved, although an endeavour has been made to bring the information up to date. A portion of Chapter XVII, on “Crystallisation and Granulation of Fertiliser Products,” has been rewritten, and it now contains the latest information on a branch of the manufacture of fertilisers which is engaging increasing interest at the present time. The application of granular fertilisers to the soil undoubtedly gives larger yields of crops than compound fertilisers, and for this reason the demand for them will increase.

June 1946

P. PARRISH.

A. OGILVIE.

FIRST FOREWORD

A BOUT a year ago I was asked by a director of a company with interests in fertiliser factories to recommend a book on the manufacture of fertilisers. I replied by sending him a copy of *Artificial Fertilisers* by Parrish and Ogilvie, but I was obliged to write my friend a note telling him that owing to important developments in the industry during the last few years, although this book was regarded as the standard work on the manufacture of superphosphate and compound fertilisers in this country, it was slightly out of date. It was with the greatest pleasure, therefore, that a few months later I received a letter from one of the Authors stating that a new edition of the book was to be published and asking me to write a Foreword to it.

Thirty years ago there was little machinery used in a superphosphate works, and such machines as were in use were of a somewhat primitive nature. In a modern superphosphate and compound fertiliser works to-day manual labour has almost entirely disappeared, and the condition of the finished products is vastly improved. The possibility of making use of machinery to a much greater extent has been brought about chiefly by improvements in the methods of mixing and treating superphosphate, which have so altered the structure of the material that it no longer pastes and clogs the machinery with which it comes in contact.

The Authors of *Calcium Superphosphate and Compound Fertilisers* have been at great pains to collect and collate details of all the recent developments in the technique of the industry throughout the world, and they are to be congratulated on the thoroughness of their researches, which will certainly be of great service to many manufacturers.

Naturally some of the information in a work of this kind must be obtained second-hand, and I imagine that some of those readers who have specialised knowledge of the trade will not agree with everything the Authors have written, but I can find no subject or method of importance to the industry which is not dealt with in this book, and I wish it every success.

In their "General Survey of the Fertiliser Position" in this country the Authors ask the question whether the development of the industry has not been restricted by the too rigid adherence of manufacturers to the water solubility test. This question presents a wide field for discussion. I should be sorry to see any departure from the present attitude of the trade. I remember the harm done to the basic slag trade, and the confusion caused in the mind of the farmer, when the citric solubility test, which, although only a relative test, was at least some criterion to the value of a slag to plant life, was dispensed with. It is to be hoped that water solubility as a test of the value of superphosphate will never be departed from in this country until it is proved that water soluble phosphate is not the quickest acting form of phosphate plant food.

SECOND FOREWORD

MY association with the calcium superphosphate industry covers a period of over fifty years. Its development has been watched by me with keen and active interest, and the various phases through which it has passed constitute indelible landmarks in my memory.

What is abundantly clear to-day is that a rural England is a definite necessity. The unfortunate migration of the populace to large cities does not appear to have been arrested, despite the warnings that have been issued from time to time. Whatever may be said about the standard of culture of the British race, it can hardly be regarded as one imparting a love of country. That a love of country, as distinct from the town, must be fostered, and with it the development of the land and agriculture, is an indispensable preliminary to the establishment of a sound nation, its economy, and security.

The book on the subject of *Calcium Superphosphate and Compound Fertilisers: their Chemistry and Manufacture*, by Messrs. Parrish and Ogilvie, has been read by me with keen interest, and it is gratifying to note that it treats of many current problems in an interesting and attractive way. The information about continuous, autoclavic and intermittent processes of superphosphate manufacture is well presented, and many novel aspects are developed.

Opinion as to the best form and analysis of N.P.K. fertilisers for specific purposes, and for application to different qualities of soil, must be divided. That a definite advance in the application of fertilisers has been made, as a result of the progress of science and the data collated in continued field trials, cannot be doubted.

The book of Messrs. Parrish and Ogilvie is particularly attractive, because it deals in detail with the economic handling, by various methods, of phosphate rock and calcium superphosphate, as indeed with the preparation of compound fertilisers. Both these aspects are peculiarly important, as affecting the economy of a fertiliser works.

The chapter on "The Structure of the British Superphosphate Industry, and the Design and Management of a Superphosphate Works" is a comprehensive one, and deals with many phases. Those relating to costs of manufacture of sulphuric acid and calcium superphosphate, and the factors affecting such costs, must be welcomed by fertiliser manufacturers and their staff generally.

Finally what is impressive is the fact that the book is happily conceived, well presented and illustrated, and withal is readable. It can confidently be recommended to the industry as one that can with advantage be consulted on many significant aspects, and will indeed repay careful study.

King's Lynn.

H. C. BROWN.

CHAPTER I

THE FERTILISER INDUSTRY, WITH PARTICULAR REFERENCE TO THE POSITION OF THE MANUFACTURE OF CALCIUM SUPERPHOSPHATE AND COMPOUND FERTILISERS

THE British fertiliser industry has many ramifications, and these are represented in Fig. 1. From this diagram it is seen that the British fertiliser industry is not alone concerned with the manufacture and distribution of inorganic chemical products designed to improve the fertility of the land, such as nitrogen, phosphoric acid and potash, but it provides by-products such as basic slag and in addition calcium carbonate, and in some cases lime, which are used largely as correctives for soil acidity.

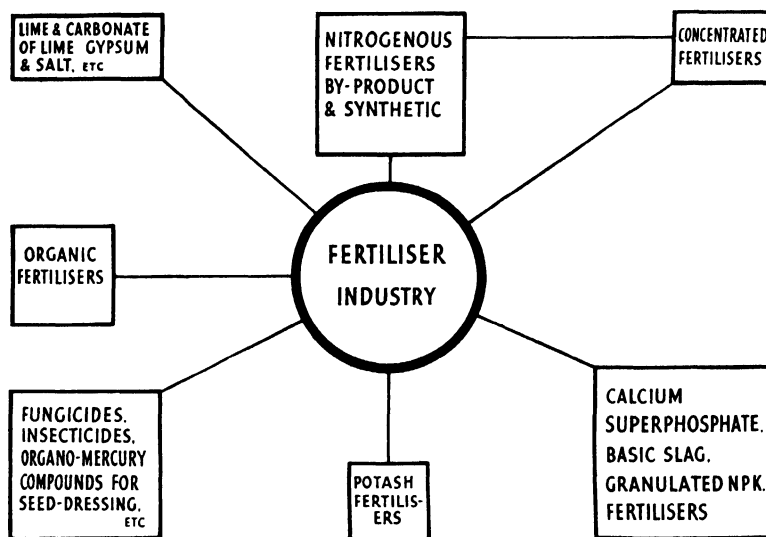


Fig. 1.—RAMIFICATIONS OF THE FERTILISER INDUSTRY

It also furnishes organic fertilisers such as bone superphosphate, dried blood, bone meal, Peruvian and fish guano, and other such products, that are calculated to improve the soil tilth, as well as supply suitable nutrients for the soil. Further, it provides fungicides, etc., the value of which before the war was estimated at £6,500,000 per year.

The synthetic ammonia industry of this country appears to be more broadly based than the calcium superphosphate section. Ammonia is derived by synthesis, using either the modified Haber or Mont Cenis or other processes. Such ammonia can be converted to nitric acid and ammonia absorbed by the latter acid, to form ammonium nitrate, which, mixed in about equal proportions with calcium carbonate (the source of which will be explained later), yields nitro-chalk.

Synthetic ammonia can also be converted to sulphate of ammonia by reaction with carbon dioxide in suitable vessels containing finely-ground anhydrite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) in suspension. In this way a solution of ammonium sulphate of about 25-30 per cent is produced, which is evaporated, crystallised out and dried to yield ammonium sulphate crystals and calcium carbonate arising at the rotary filter presses is yielded as a by-product. This is dried and used in various ways, one of which is as a component of nitro-chalk.

Anhydrite can be treated with clay and silica to form cement by the dry process, and the resulting SO_2 can be converted to sulphuric acid by the contact process. The strong sulphuric acid in question can, by the Dorr strong acid process (*see* page 160), react on phosphate rock to produce phosphoric acid. This phosphoric acid can be neutralised with gaseous synthetic ammonia or liquor ammonia, and ammonium phosphates—monoammonium phosphate or diammonium phosphate—can be produced.

This expresses succinctly the salient features of the synthetic ammonia industry of this country. A more detailed indication of what is possible will be given later.

As regards potash salts, of which 75,000 tons as K_2O was used in the period 1st July, 1938, to 30th June, 1939: unfortunately, this country is not too well placed. English capitalists are interested in Palestine Potash, Ltd., which has supplied more than fifty per cent of this country's requirements of muriate of potash during the war years, 1940-45. Other supplies have been derived from America, Russia and Spain. Following the European peace, doubtless the importation of relatively large quantities of potash in the form of muriate of potash (30 per cent K_2O) and sulphate of potash (48 per cent K_2O) from France and Belgium, where works exist for the conversion of muriate of potash to sulphate of potash, will be resumed.

Phosphatic (P_2O_5), Nitrogenous (N_2) and Potassic (K_2O) Fertilisers

Trade in these fertilisers cannot any longer be regarded as the prerogative of the calcium superphosphate industry. There are now two sources of supply. The older source of supply is the calcium superphosphate manufacturers, who have from their inception produced superphosphate and gradually developed the preparation of compound fertilisers for specific soils, and for specific crops. They have improved the manufacture of their products and are now concerned not only to ensure the supply and distribution of the most suitable fertilisers, from the point of view of their chemical composition, but are anxious to meet the requirements of the farmers and horticulturalists as regards physical characteristics and efficiency of application.

The other supplier is the manufacturer of synthetic ammonia, who not only produces sulphate of ammonia, but prepares complete chemical fertilisers in various forms at the synthetic ammonia factory, where ammonia and phosphoric acid (cheaply produced) can be combined as monoammonium phosphate or diammonium phosphate, and where potash can be incorporated in various forms as represented in the table below:—

TABLE 1

Synthetic Fertiliser Products and Mixtures Containing Nitrogen

Plant Food Constituents.	Fertiliser.	
	Compounds.	Mixtures.
Nitrogen	Ammonium nitrate. Calcium nitrate. Sodium nitrate. Urea. Ammonium sulphate.	Nitro-chalk.
Nitrogen and phosphoric acid.	Monoammonium phosphate. Diammonium phosphate. Urea phosphate.	Ammophos. Phosphazote. Ammoniated superphosphate.
Nitrogen and potash	Potassium nitrate.	Potazote. Kali ammonsalpeter.
Nitrogen, phosphoric acid and potash.	—	Nitrophoska. Ammophoska. Miscellaneous mixtures.

From the above table it will be seen that the chief synthetic nitrogenous fertilisers come under two headings, namely compounds or mixtures. The products of the first class are chemical compounds and contain nitrogen as the only plant nutrient, or nitrogen in combination with either potash or phosphoric acid. Those of the second class consist of mixtures of products of the first class, or of mixtures of these with other materials, which may or may not contain potash and phosphoric acid.

It is clear that a large number of fertiliser mixtures can be prepared in the above manner. It is not proposed to make more than a brief reference to these various products.

Ammonium Nitrate.—This is prepared by the conversion of synthetic ammonia to nitric acid, and the distillation of ammonia from liquor ammonia into the nitric acid so manufactured, or by direct neutralisation of liquor ammonia and nitric acid. Such neutralisation has to be conducted in a special tower, designed to avoid a violent reaction with consequent loss of ammonia. The neutralised solution is settled to deposit ferrous hydrate and the clear solution is subjected to filtration, and concentration in a vacuum evaporator. The concentrated solution passes to automatic rocker crystallisers, where the crystals and solution slowly flow from one side of the crystalliser to the other. Such movement promotes the formation of a pure and uniform size of crystal, without mother liquor occlusion.

The magma is then discharged to suitable centrifugals and the moisture content is reduced to 4 per cent. Subsequently the ammonium nitrate crystals are dried by passage of warm air through the drying apparatus and the salt emerges containing 0.1 to 0.05 per cent of moisture. The dried salt is screened and is discharged to barrels, ready for dispatch. Ammonium nitrate contains equal parts of nitrate and ammoniacal nitrogen—the total nitrogen content being 34-35 per cent. It is hygroscopic, and unfortunately it cakes. Its physical condition can be improved by granulation or by mixture with certain materials, such as ammonium sulphate or calcium carbonate, or even kaolin has been used with a view to avoiding detonation, and imparting other desirable attributes.

It should be observed here that the properties of ammonium nitrate as a fertiliser have been studied by Ross, Adams and Yee¹ and large-scale tests have been undertaken. These studies reveal that ammonium nitrate can be produced and stored in a satisfactory form for direct use as a fertiliser, by granulating the product to give particles of 8 to 16 mesh, drying to 0.2 per cent moisture content, treating with 3 per cent of a suitable conditioning agent and storing in waterproof bags. The conditioning agents suggested are kaolin and various types of kieselguhr.

The well-known *nitro-chalk* is a mixture of ammonium nitrate and calcium carbonate, and contains 15½ per cent of nitrogen, half as ammonia and half as nitrate.

Calcium Nitrate.—This product was originally manufactured in Norway, and contained 13 per cent of nitrogen. The actual nitrogen content depends on the purity of the calcium carbonate used and whether any free moisture is removed by drying. Usually, calcium nitrate contains 4 molecules of water of crystallisation, but it is possible to reduce this combined moisture to about 2 molecules.

Calcium nitrate absorbs water even more rapidly than ammonium nitrate, and to remedy this defect it is desirable to prepare a granulated product. Moreover, it is preferable to store it in bags having waterproof liners. To overcome the unpleasantness of handling the grey product, white calcium nitrate has recently been manufactured, by a process calling for the addition of about 5 per cent ammonium nitrate. The granules of this product are smaller and more spherical than the grey form of nitrate of lime. White nitrate of lime contains 15½ per cent nitrogen, one per cent as ammonia and 14½ per cent as nitrate.

Sodium Nitrate.—Possibly under any new international arrangements the supply of this product will be assigned to Chile. But it is an easy matter to prepare the product by neutralisation of nitric

¹ *Journal of Industrial Engineering Chemistry*, December, 1944, p. 1088.

acid with a solution of soda ash, evaporating the neutralised solution, crystallising out and centrifuging the crystals so obtained. In the last war sodium nitrate was produced by the double decomposition of sodium chloride and ammonium nitrate.

Urea.—Urea can be synthesised from ammonia and carbon dioxide. Indeed, ammonium carbamate (one of the products associated with commercial ammonium carbonate) is possibly an intermediate product. The experiments conducted at temperatures between 115° C. and 150° C. by Fichter and Becker revealed that the optimum conversion to urea occurred at 135° C. Moreover, it was found that the density of loading of the container was important, and that the highest yield coincided with the highest loading density. The results at 135° C. are shown in the following table :—

TABLE 2

Conversion of Carbon Dioxide and Ammonia to Urea
(Composition of the charge is that equivalent to ammonium carbamate.)

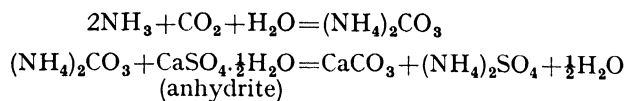
Charge density.	Time of heating.	Yield of urea.
Grams.—c.c.	Hours.	Per cent.
0.0324	24	Trace.
0.054	24	13.6
0.081	24	28.0
0.108	48	31.2
0.216	48	36.8
0.432	48	36.7
0.432	72	40.0
0.649	96	40.64

The problem of attempting to increase the yield of urea formed from ammonium carbamate has been a captivating one. It has been suggested that the addition of dehydrating agents to remove the water formed in this synthesis might be advantageous, but trials showed that dehydrated magnesium sulphate in the gaseous and the liquid phases, and calcium chloride in the gaseous phase, reduced the conversion. The introduction of anhydrous ammonia up to nearly 300 per cent of that combined as carbamate of ammonia gave conversions between 81 and 85 per cent of the carbamate of ammonia to urea. To-day urea is produced from liquid carbon dioxide and liquid ammonia, heated to a high temperature under pressure. The fused mass is leached with water and the solution is distilled, filtered and evaporated to yield urea. The nitrogen of this product exists as an amide, which is an organic form. Thus, like cyanamide, they form, as it were, intermediate products between the ammonia fertilisers and those organic manures which possess animal or vegetable origins.

Recently urea has been produced from concentrated gas liquor by a method developed by C. Koepfel.

Ammonium Sulphate.—The largest ammonium sulphate works, such as Oppau and Merseburg in Germany, the I.C.I. in England, and Toulouse in France, have dispensed with the use of sulphuric acid, and now use either gypsum or anhydrite. Each of these products is finely ground, maintained in suspension in about twice its weight of water by agitation, and ammonia and carbon dioxide are passed into the gypsum or anhydrite water suspension. Ammonium carbonate is initially formed, and this reacts with the calcium sulphate to form calcium carbonate and ammonium sulphate, the

latter of which passes into solution. The double decomposition is completed in from six to nine hours. The following indicates the nature of the reactions:—



The magma containing calcium carbonate and about 25-30 per cent of ammonium sulphate is filtered, ammonium sulphate solution is evaporated in vacuum evaporators with specially arranged calandria, the ammonium sulphate is centrifuged, dried and discharged to the heap. The mother liquors are added to the water in which the next batch of gypsum or anhydrite is suspended.

Ammonium Phosphates.—As the orthophosphates are, generally speaking, those of major importance in the fertiliser industry, reference will be confined to these.

Orthophosphoric acid is tribasic, reacting with ammonia to form three ammonium phosphates, namely, mono-, di- and triammonium phosphate. Monoammonium phosphate is slightly acid in reaction, diammonium phosphate is slightly alkaline, and triammonium phosphate is strongly alkaline. These three compounds vary in stability and for this reason for commercial purposes only monoammonium and diammonium compounds are manufactured.

(A) *Monoammonium Phosphate.*—In this country phosphoric acid is prepared by what is known as the “wet” method, that is, by the action of sulphuric acid on phosphate rock, as is described in detail in Chapter XIII. The phosphoric acid manufactured by the wet method has a maximum concentration of 25-30 per cent.

To manufacture monoammonium phosphate, gaseous ammonia is introduced to the phosphoric acid (prepared in the “wet” way) in open vessels, to the point where the solution reacts yellow to methyl orange and red to methyl red. The exothermic heat of reaction is adequate to raise the temperature of the liquid to boiling-point. The iron and aluminium phosphates present are precipitated and lead to the formation of a slurry, which is difficult to filter. The whole mass, therefore, is reduced to dryness by feeding it into a rotary kiln, the temperature of which is maintained below 120° C. Because of the continuous agitation to which the material is subjected a granular product, capable of being applied to the soil by drills, is produced.

In Europe a modified process has been introduced. A solution of monoammonium phosphate in sulphuric acid is obtained by replacing with ammonium sulphate slightly less than one-third of the sulphuric acid in treating phosphate rock. The reaction occurring when the phosphate rock is treated with one equivalent of ammonium sulphate to two of sulphuric acid, may be represented thus:—



The above magma needs to be filtered to remove the calcium sulphate and any free acid associated with the liquid monoammonium phosphate is neutralised with free ammonia. The precipitated iron and aluminium phosphates that settle out are removed by filtration and the filtrate is concentrated to crystallise out monoammonium phosphate. By varying the proportions of the two salts, monoammonium phosphate as such, or a mixture of the latter with sulphate of ammonia, can be produced. The iron and aluminium phosphate sludge can be sold as a crude fertiliser. Calcium sulphate can be made into a suspension and converted to ammonium sulphate by introducing ammonia and carbon dioxide. The calcium carbonate resulting from this latter process is used in the manufacture of nitro-chalk, or is dried and applied to the land. The commercial product contains 56.5 per cent of P₂O₅. Occasionally it is sold with ammonium sulphate, thus raising the proportion of nitrogen to phosphoric acid.

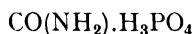
(B) *Diammonium phosphate.*—The production of diammonium phosphate for use as a fertiliser possesses certain merits, as contrasted with the mono- compound, because (a) it contains 25 per cent of ammonia, as against the mono- compound of approximately 14 per cent ammonia, and (b)

there is clearly a corresponding reduction of manufacturing costs per unit of plant food. The process normally adopted for the manufacture of diammonium phosphate is to add concentrated phosphoric acid to a solution of the salt, saturated at, say, 20° C., until the solution changes the colour of bromocresol purple, or until the phosphoric acid content of the solution is increased by about one-third.

Gaseous ammonia and phosphoric acid are then introduced at the same time in the proportion of 1.5 molecules of the former to one molecule of the latter, the rate of addition being such that a temperature of 80-90° C. is not exceeded. The addition of ammonia and phosphoric acid is continued until the phosphate content of the solution is approximately doubled. The solution is then cooled to 20° C. and ammonia is introduced until a diluted representative sample of the solution reacts neutral to cresol red.

Diammonium phosphate crystals prepared under the above conditions are centrifuged and subsequently dried at 60° C. It is usual to add the mother liquor to the next batch for re-use in the process. The commercial product sold on the continent contains 53.4 per cent of P₂O₅. Ammophos is sold in the U.S.A. in two grades, having respectively 11 per cent of nitrogen and 48 per cent of phosphoric acid, and 16.5 per cent nitrogen and 20 per cent phosphoric acid. Leunaphos is a mixture of diammonium phosphate and sulphate of ammonia, and contains 20 per cent of nitrogen and 20 per cent of phosphoric acid.

Urea Phosphate.—This is merely an addition compound, and its formula is :—



It is not widely used at the present time, having regard to the reduced number of products rendered necessary by the exigencies of the war. It can be manufactured by dissolving an equivalent quantity of urea in 60-85 per cent phosphoric acid. Heat is applied, if found necessary, and then cooling must be resorted to, with stirring, in order to deposit the salt in the form of orthorhombic crystals.

Urea phosphate prepared in the above manner contains approximately 17.8 per cent of nitrogen and 44.8 per cent of P₂O₅. It is readily soluble in water and it hydrolyses to give an acid solution.

Potassium Nitrate.—This product can be prepared in several ways. Indeed, many of the Chilean nitre deposits contain from 5 to 7 per cent, and in some few cases as high as 17 per cent of potassium nitrate.

Potassium nitrate may be prepared by treating a solution of calcium nitrate with potassium sulphate. From the resulting solution the calcium sulphate is removed and it is then concentrated to yield a high-grade potassium nitrate.

A more recent process resides in the treatment of potassium chloride with nitric acid (35 per cent) at 40° C. or below, cooling to -12° C. to admit of the crystallisation of the potassium nitrate. The mother liquor is neutralised with ammonia to yield ammonium chloride.

As regards the mixtures which have been referred to in Table 1, little need be said, as ready means for their preparation are apparent.

It is evident from the sales list published by Imperial Chemical Industries, Ltd., that they have not made any elaborate provision for the production of chemical compound fertilisers, but have adopted a method which is marked by consummate simplicity. They use only the two major products which they manufacture, *viz.*, ammonium sulphate and ammonium phosphate, and mix these in suitable proportions with muriate of potash, sulphate of potash, 30 per cent potash salts and rock phosphate, by a special process, in the manufacture of their Concentrated Complete products. By the process in question uniformity of composition is ensured. Subsequently, the fertilisers are prepared in granular form to obtain good storage qualities, regularity in distribution and clean handling. Moreover, they have taken a lead from the principal makers of feeding stuffs, who for some time have offered for sale what they have termed "Declared compounds." This means that they have not only declared the analyses, as legally required of them, but have also voluntarily guaranteed the actual ingredients from which their cakes, cubes and meals are derived.

Apparently, with the introduction of concentrated complete fertilisers, Imperial Chemical Industries, Ltd., resolved that the same advantages should be open to purchasers of their compound fertilisers. Below will be found the analyses and ingredients of these fertilisers:—

TABLE 3¹*Declared Fertilisers—Analyses and Ingredients*

The table below sets out the actual amounts of each ingredient used for the manufacture of I.C.I. Concentrated Fertilisers.

C.C.F.	Analysis.				Ingredients (lb.) used in the manufacture of 1 ton.					
	N	P ₂ O ₅		K ₂ O	Sulphate of Ammonia	Ammonium Phosphate	Muriate of Potash	Sulphate of Potash	30% Potash Salts	Phosphate Rock
		Sol.	Insol.							
No. 1	% 12·4	% 12·4	% 0·2	% 14·9	lb 1,050	lb. 508	lb. 334	lb. 348	lb. —	lb. —
No. 2	10·3	10·3	0·2	20·7	872	420	464	484	—	—
No. 4	10·2	20·4	0·4	10·2	630	840	—	—	770	—
No. 5	8·0	16·0	5·5	16·0	480	652	718	—	—	390
No. 6	7·5	26·0	6·0	7·5	184	1,058	—	—	560	438
No. 7	6·5	22·5	3·0	13·0	160	916	—	—	971	193
N.P. A	13·8	41·4	0·9	—	506	1,734	—	—	—	—
B	17·9	17·9	0·4	—	1,512	728	—	—	—	—
C	15·6	31·2	0·7	—	950	1,290	—	—	—	—

Example:—

One ton of C.C.F. No. 1 contains :

1,050 lb. of sulphate of ammonia
 508 lb. of ammonium phosphate
 334 lb. of muriate of potash
 348 lb. of sulphate of potash

Total 2,240 lb.

¹ The above analyses and ingredients of equivalent mixtures are taken from the I.C.I.'s Declared Fertiliser List.

Equivalent Mixtures

The table below shows the quantities of ordinary ingredients—sulphate of ammonia, superphosphate, sulphate of potash and 30 per cent potash salts—needed to make up the equivalent in plant food of 1 cwt. of each *Concentrated Fertiliser*. It will be seen that the quantities range from 201 to 406 lb.

	C.C.F. No. 1	C.C.F. No. 2	C.C.F. No. 4	C.C.F. No. 5	C.C.F. No. 6	C.C.F. No. 7	NP A	NP B	NP C
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
Sulphate of Ammonia (20·6% N)	67	56	56	44	41	35	75	97	85
Superphosphate (14% P ₂ O ₅)	99	82	163	128	208	180	331	143	250
Phosphate Rock (26% P ₂ O ₅)	—	—	—	24	26	13	—	—	—
Sulphate of Potash (48% K ₂ O)	17	24	—	—	—	—	—	—	—
Potash Salts (30% K ₂ O)	28	39	38	60	28	49	—	—	—
Total	211	201	257	256	303	277	406	240	335

Example:—

To supply the same quantities of nitrogen, phosphates and potash as are contained in 1 cwt. (112 lb.) of C.C.F. No. 1, we require a total of 211 lb. if we use sulphate of ammonia, superphosphate, sulphate of potash and 30 per cent potash salts.

The justification for dealing at some length with the concentrated fertiliser branch of the synthetic nitrogen industry of this country lies in the success which it has achieved. Lord McGowan, speaking at the Eighteenth Ordinary General Meeting of I.C.I., Ltd., gave some interesting information about the activities of his firm during the World War. He said :

“We were responsible for turning out over half a million tons of sulphate of ammonia a year, and we did this without neglecting the production of other fertilisers made at Billingham, e.g., nitro-chalk and complete fertilisers. Indeed, the yearly output of these together was stepped up from 160,000 tons in 1939 to over 260,000 tons in 1944. These fertilisers were essential: without them neither the ‘Grow More Food’ campaign of our farms, nor the ‘Dig for Victory’ one in our gardens, could have succeeded as they did.”

It is hoped that undue prominence has not been given to the concentrated complete fertiliser branch of the synthetic ammonia industry.

The calcium superphosphate industry has associated with it a synthetic ammonia factory at Flixborough, and it is certain that it will keep itself alive to the importance of current developments. In our survey of the fertiliser industry we must continue to examine briefly the other branches of the industry, in order to present something like a complete verbal picture.

Organic Fertiliser Industry.—The organic fertiliser industry is an important one, and has been under the control, during the war, of a semi-official organisation of the name of Fabon, Ltd., which has administered affairs to general satisfaction. This industry is not alone concerned with fertiliser products, but produces fat, tallow, glues, size, gelatine and osseine. As is seen, some of these latter products are of importance from an industrial point of view: others from the viewpoint of foodstuffs.

It is an industry that is likely to suffer in the matter of production by reason of a dearth of raw materials. The killing of large numbers of cattle earlier in the war, because foodstuffs were not too plentiful, and the inability to obtain Indian bones with the usual facility, may have reduced the volume of production during 1943 and 1944.

The word "organic," used in conjunction with fertilisers, doubtless creates a certain amount of fascination. But there is little disposition for organic fertiliser enthusiasts to attack artificial fertilisers, just as enthusiasts in the use of artificial fertilisers are disinclined to ignore the advantages of organic fertilisers. There are signs of increasing interest in "organics" by those responsible for agricultural research, and it is felt that an examination of many of the problems of the industry cannot but be fruitful of good results, and that all will profit by the investigation.

Lime, Carbonate of Lime, Gypsum and Salt Industry.—This is a branch of the fertiliser industry which has assumed increasing importance during the war. Indeed, the subsidy given under the Land Fertility Scheme some seven or eight years ago has afforded greater prominence to the advantages of carbonate of lime and lime as correctives for soil acidity. These are substances which in themselves are not plant foods, and yet it is necessary that they should be applied to the soil in order to render it more amenable to cultivation, or to release or bring into action the stored-up reserves in the soil. Sir A. D. Hall says: "The regular use of some form of lime or chalk was part of the accepted routine of farming as early as we possess any records of British agriculture, and among the manures it figures in all books of the sixteenth and seventeenth centuries. In fact, "black and white," dung and lime, were the only manures employed by the great mass of farmers until well into the nineteenth century."

The large producers of lime are Imperial Chemical Industries, Ltd., and the Cement Marketing Co., Ltd. One treats limestone in the manufacture of lime: the other subjects chalk to the so-called process of burning, which is really a decomposition process. A good quality of lime should contain not less than 92 per cent CaO, with not more than 5 per cent of unburnt limestone or chalk. It has not been an easy matter to maintain a high standard of quality during the war, for obvious reasons.

Fairly large quantities of impure calcium carbonate are produced in water-softening processes, and in many other industries, and it is profitable to pass these residues through filter presses, subsequently to dry them in rotary dryers and sell the dried carbonate of lime under the Land Fertility Scheme for application to the land.

Gypsum is used to render certain fertilisers dry and friable, and for some time this material has been applied to leguminous and such other crops as are specially dependent upon potash, when it has exerted a beneficial effect. This is on the principle that the solution of calcium sulphate arising from the gypsum will attack zeolites containing potash and will thus bring potassium sulphate in solution in the soil water.

The use of salt alone, or as an adjunct to other fertilisers, is a common farming practice: indeed, it is usual, in growing mangolds, to apply in many cases as much as 2 or 3 cwt. of salt per acre as a top dressing, with or without nitrate of soda. In the "fens" of Lincolnshire potatoes are generally grown with calcium superphosphate, farmyard manure and a liberal dressing of salt.

Potash Industry.—Reference has already been made to this industry, but a few further words should be said. The important deposits in Alsace were discovered in 1904. The origin of these natural deposits is interesting. They are supposed to be the primary and secondary residues of a dried-up sea, although there are various theories to account for the great depth of the salt strata. The potash fertilisers which are found on the English market are:—

	Pure potash (K ₂ O). Minimum guarantees.
Muriate of potash	50·4 per cent.
Sulphate of potash	48·6 ..
Potash salt	30·0 ..
Potash salt or kainit	20·0 ..
Kainit	14·0 ..

TABLE 4¹*Average Composition of Potash Salts*

GRADES.	Sulphate of Potash (K ₂ SO ₄).	Chloride of Potash (KCl).	Sulphate of Magnesia (MgSO ₄).	Chloride of Magnesia (MgCl ₂).	Sodium Chloride (NaCl).	Sulphate of Lime (Gypsum) (CaSO ₄).	Insoluble in Water.	Water (H ₂ O).	Corresponding amount of Pure Potash (K ₂ O).	Guaranteed Minimum of Pure Potash (K ₂ O).	Total Chlorine (Cl).	For 100 parts Potash (K ₂ O) there are present parts of Sodium Chloride.
Kainit 14%	—	23.7	—	0.1	62.3	2.5	10.2	1.1	14.9	14.0	49.1	418.1
Kainit 20%	—	33.2	—	0.1	53.8	2.1	9.4	1.3	20.9	20.0	48.5	257.4
Potash Salt 20% (also sold as Kainit 20%)	—	33.3	12.0	4.2	40.2	2.1	4.0	4.2	20.9	20.0	40.3	192.3
Potash Salt 30%	—	48.6	10.2	4.2	26.2	2.2	3.5	5.1	30.7	30.0	42.1	85.3
Sulphate of Potash - Magnesia 26%	50.4	—	28.0	—	3.5	3.4	7.6	7.1	27.2	26.0	2.1	12.9
Muriate of Potash— Purity 80 85%	—	83.5	0.4	0.3	14.5	—	0.2	1.1	52.6	50.4	48.5	27.6
„ 90 95%	—	91.7	0.2	0.2	7.1	—	0.2	0.6	57.8	57.0	48.1	12.3
Sulphate of Potash - Purity 90%	90.6	1.6	2.7	1.0	1.2	0.4	0.3	2.2	49.9	48.6	2.2	2.4
„ 96%	97.2	0.3	0.7	0.4	0.2	0.3	0.2	0.7	52.7	52.7	0.6	0.4

¹ *Potash Fertilisers: Their Practical Use*, by G. A. Cowie, M.A., B.Sc., F.R.I.C. (United Potash Co., Ltd., London).

Table 4 gives the average chemical composition of potash salts. During the World War potash salts have been in short supply, and recourse has been had to the recovery of potash from blast furnace flue dust, while during the last three or four years we have been indebted to Palestine Potash, Ltd., America, Russia and Spain for our supplies.

Fungicides, Insecticides, Organo-Mercury Compounds, etc., Industry.—This is an important branch of the fertiliser industry, and has grown, and will continue to grow. Many substances have been recommended for eradicating weeds from cereal crops, but not all have stood the test of time. It is known that copper sulphate, powdered cyanamide and sulphuric acid have survived. Copper sulphate is easy to apply and handle, but its use is limited to a few weed species, such as yellow charlock, etc. Cyanamide can control a wide range of weeds, always provided the powder is applied under such conditions that the material is kept in contact with the weed, and is not washed away too early by rain.

Sulphuric acid has been applied effectively for some ten years now, and is successful in dealing with charlock and potato haulm preparatory to lifting the crop.

But G. E. Blackman, B.A.,² has dealt with “Alternatives to sulphuric acid for the control of annual weeds in cereals.” It is desirable that this contribution should be studied. He remarks that where copper sulphate has been used for yellow charlock in spring cereals, a change to copper chloride has many advantages. Apparently, copper chloride acts quicker, and is therefore less dependent on fine weather after spraying for good results. Copper chloride, in contrast with sulphuric acid, maintains its effectiveness even when spraying is delayed until the charlock is in flower. It is claimed that the superiority of copper chloride over copper sulphate holds for all annual weeds.

² *Fertiliser Journal*, Vol. 30, No. 9, p. 191.

Copper sulphate, even at concentrations of 8 per cent, does not kill the most aggressive weeds of lighter soils—white charlock, runch and white radish. On the other hand, copper chloride may give a fair and even control at strengths of 2 to 4 per cent, provided that white charlock is sprayed in the four-leaf seedling stage.

Research under grants from the Ministry of Agriculture Research Council, undertaken at the Imperial College, has been fruitful of good results. Two phases of the work in which most progress has been made are concerned with the relative merits of copper salts and the value of dinitro-ortho-cresol compounds. The latter can be abbreviated to D.N.O.C. It is an active constituent of oil wash used for late winter spraying of fruit trees, and gives the spray its characteristic bright yellow colour. D.N.O.C. is a starting-point for yellow dyestuffs, and its skin and clothing-staining properties give little surprise.

It has been demonstrated that copper chloride is much superior to copper nitrate, and this, in turn, is superior to copper sulphate, alone or mixed with agricultural salt. The sodium salt of D.N.O.C. is far less effective than the ammonium salt, but the efficiency of the sodium salt can be greatly improved by the addition of ammonium sulphate. It should be noted that D.N.O.C. compounds, when dry, are highly inflammable, and for this reason it is usual to dispatch them as water pastes, containing up to 50 per cent concentration. Old clothes should be worn whenever they are being applied, together with gum boots, rubber apron and rubber gloves.

An entirely new revolutionary type of selective weed-killer for agriculture has been developed by I.C.I., Ltd. This weed-killer, known as Methoxone, is a growth substance of the plant hormone type. The merit of the new weed-killer is that it will kill the charlock and many other weeds without harming the cereal crops. The trials already made have shown that when it is applied at the rate of 1 lb. per acre weeds such as yellow charlock, white radish, corn buttercup and pennycress, growing in corn, are killed, but the crop is unharmed. Large increases in the yield of wheat, barley and oats are predicted. But we should not overlook sodium chlorate as an effective destroyer of fungus and unwanted vegetation, and being non-toxic it is preferred by some to calcium arsenate and other arsenicals, although the latter appear to be popular for specific purposes.

Vegetable products such as rotenone, pyrethrum and nicotine are in constant use, and indeed appear to be gaining in popularity. Certain cyanides are used as fumigants for glasshouses: emulsified tar oils are used for winter washes and organo-mercury compounds are used as seed dressings, to kill seed-borne fungi, the best-known of which are smuts, the spores of which may be present on the grain of wheat, barley and oats.

For soil fumigation, super-whizzed naphthalene is strongly recommended in some quarters, whereas for harmful bacteria and insects which attack tender plants, Ster-Izal appears to be gaining in popularity. But steam treatment is equally favoured for this purpose, and recourse is often had to the irrigation of the soil by a solution of formaldehyde or cresylic acid. In this connection, however, Sir A. D. Hall¹ has pointed out that much further work is yet required before soil sterilisation can be effected with certainty. There are certain organisms, large as compared with bacteria, definitely belonging to the animal kingdom, and called, from their simplicity of structure and primitive type, protozoa. The protozoa, of which three main groups are found in the soil—amœbæ, ciliates and flagellates—are single-cell organisms, varying in size from 5 to 50 μ .

Brief reference should be made to "Gammexane,"² an insecticide with outstanding properties. It was established, after much experimental work by the I.C.I., that the insecticidal action of hexachlorocyclohexane (666 for short) was due almost entirely to the presence of *gamma* 1, 2, 3, 4, 5, 6, hexachlorocyclohexane, now known as Gammexane. This, the active principle of 666, is present to the extent of 10 to 12 per cent in the crude material. There was, during the war, a need for an insecticide as a substitute for ground derris. This demand was satisfied by producing finely-divided powder containing 20 per cent of crude 666 and 80 per cent of gypsum, which was further diluted with selected materials to give insecticidal powders for use on crops. Gammexane, unlike many insecticides, has proved to be exceptionally suitable to high temperatures. Apparently, considerable acreages of weed pests have been successfully treated for the control of pests by Gammexane. It is also highly effective against bed bugs, and as a mosquito larvicide. It also attacks effectively the pests of stored-up products such as green weevil.

¹ *The Soil* (John Murray), p. 236, *et seq.*

² *The Industrial Chemist*, April, 1945, p. 173, *et seq.*

It is estimated that £1,500,000,000 is the value of the food lost each year by pests.¹ D.D.T. is used on a large scale, sprayed by tractors and aeroplanes, for grains, but is still used cautiously for pastures. With fruit crops, since D.D.T. kills off ladybirds, mites normally harmless become a devouring plague. Swiss D.D.T. and British Gammexane are gaining pest mastery. D.D.T. is not effective against cotton boll weevil, but Gammexane can deliver the U.S. cotton crop from this.

Calcium Superphosphate Industry

Coming now to the superphosphate industry, it should be made clear that this book treats of the various unit processes involved in the manufacture of calcium superphosphate: it refers in detail to the compounding of manures and gives particulars of the current practice (1945) in the manufacture of granular compound fertilisers.

It will be interesting to the trade to know that granulating plants have been erected, or are in course of erection, capable of producing annually half a million tons of granular fertilisers. This progressive step is one on which the industry is to be congratulated. But there are still problems to be solved, and it occurred to the authors that these should be outlined in what follows.

It has long been accepted that calcium superphosphate reacts on the soil with great rapidity. Heavy and acid soils react in this respect more rapidly than light and alkaline soils. It has been found that if superphosphate is spread on the surface of the soil, without being forked in, the phosphoric acid will penetrate only 1 to 1½ inches into the soil. The cause of this fixation is the formation of water-soluble compounds between the free phosphoric acid of the monocalcium phosphate and the basic matter in the soil, such as iron, alumina, lime, etc. Further, hydrolysis of the monocalcium phosphate to insoluble products occurs. The result is that the water-soluble compounds of a superphosphate have little or no direct fertilising effect. This would not constitute a defect if the phosphoric acid in these compounds were easily assimilated by the plant roots, because in such circumstances the superphosphate would possess the advantage, as contrasted with other water-soluble phosphatic fertilisers, that its phosphoric acid is more evenly distributed in the soil. Unfortunately, in practice the foregoing is not realised. The new products formed with iron and alumina are at first citrate-soluble, but after a time, and especially after periods of drought, they lose their citrate-solubility and consequently their fertilising value is reduced. This loss of solubility occasionally takes place so rapidly that a soil known by analysis to require phosphoric acid has revealed no increase of yield when fertilised with the normal quantity of superphosphate. Fixation and reversion into insoluble compounds is more marked in acid soils, because iron and alumina are present in a more active form than in alkaline soils. Even in neutral or alkaline soils having little, if indeed any, iron, fixation of the water-soluble phosphoric acid occurs fairly rapidly, although slower than in acid soils. This probably depends on hydrolysis and on the formation of dicalcium phosphate and hydroxyl apatite, which latter compound is insoluble to plants.

That the phosphoric acid content of superphosphate is constantly fixed in the soil, is shown by the fact that the quantity of phosphoric acid absorbed by a plant during the first year seldom exceeds 40 per cent of the total used, and may even be as low as 15 to 25 per cent. In acid soils it is even lower than the latter figure. Clearly, a modern fertiliser should be more efficient than this. That the superphosphate industry must consider methods by which to reduce or otherwise avoid the fixation of phosphoric acid, seems obvious.

Lest there should be any doubt as to what calcium superphosphate is, the authors will quote from their article on "Present-day technique in the manufacture of calcium superphosphate."²

"At this juncture it is interesting to ask the question: What is calcium superphosphate? Hitherto it was held to be a system not necessarily in equilibrium, composed of a liquid phase and several solid phases, the former consisting of water and free phosphoric acid. More recent work has been undertaken by J. W. Hill and his collaborators at the United States Bureau of Chemistry and soils. X-ray diffraction spectra were obtained of pure specimens of all the more important compounds likely to be present in the solid phase, and these individual spectra compared with the composite one given by calcium superphosphate. The results finally obtained were positive enough. It was found that anhydrous calcium sulphate and monohydrated monocalcium phosphate were predominant constituents, anhydrous monocalcium phosphate being absent, or present in minute quantity, while samples of calcium sulphate, in which the hemi-hydrate or the di-hydrate of calcium sulphate were found, were either old materials, or materials prepared with a deficiency of sulphuric acid.

¹ *News Chronicle*, 30th May, 1946.

² *Fertiliser, Feeding Stuffs and Farm Supplies Journal*, July 1st and 15th, 1936.

“What was significant about this research was the remarkably fine state of division of the solid constituents of superphosphate. The closeness with which the particles are inter-associated explains the failure of all attempts to detect the individual constituents microscopically. Practical experience has shown that calcium sulphate in superphosphate discharges a far more positive role than that of a mere loading agent, its behaviour being attributable to its very fine state of division.

The view has been held in this country, somewhat tenaciously, that there is no evidence that manufacturers have reason to question the wisdom of accepting water-solubility as the only criterion for soluble phosphoric acid under the Fertiliser and Feeding Stuff Act regulations. This view may call for further consideration at an early date, as it may well be that developments during the World War may be such as to indicate that too implicit an adherence to water-solubility may be a retrogressive step.

Certainly, one way of avoiding insolubility and reversion of the superphosphate in the soil is to modify its chemical composition. The importance of all manufacturers preparing their phosphatic fertilisers in the most suitable form for utilisation by the soil, to the maximum degree of effectiveness, need hardly be stressed.

Granulation of N.P.K. or other mixtures is a step in the right direction, because there appears to be important evidence that if granular N.P.K. fertilisers are placed in rows of the right depth, and adjacent to, but not in contact with, the seed, the increased yield of crop is surprising. The more contiguous the fertiliser is to the seed, provided contact is avoided, the better are the results.

But it is conceivable that even better results may be obtained from a citrate-soluble phosphate, that is, dicalcium phosphate, ($\text{CaH}_2\text{P}_2\text{O}_8$), than from ordinary superphosphate itself. And if this is the case, then it would be desirable to produce dicalcium phosphate for incorporation in granular N.P.K. fertilisers when the maximum effectiveness in application is likely to be reached. If dicalcium phosphate is to be the fertiliser of the future, how is this product to be manufactured in the cheapest and most efficient manner? This would appear to be the pressing question of the hour. Shall calcium superphosphate be manufactured by present methods and mixed with crude ammonium bicarbonate or reacted upon with phosphate rock up to the dicalcium stage?

On the other hand, it is conceivable that dicalcium phosphate manufactured in the above way would be ready for incorporation with potash and sulphate of ammonia, in the production of a granular N.P.K. fertiliser. These are aspects which can best be decided by experimental manufacture and extensive trials of the resulting products. Such a method as is indicated would retain the sulphuric acid method of treatment of the phosphate rock, and represent the best use of the plant and capital of the superphosphate manufacturer.

But one cannot be blind to the experimental evidence of other countries. In the first edition of this book reference was made to laboratory-scale experiments by the Bureau of Soils, which had revealed that almost the whole of the fluorine can be removed, either by heating rock phosphate to $1,400^\circ\text{C}$. in the presence of silica and steam, or by passing it in intimate contact with steam in indirect arc furnaces. Over 80 per cent of the phosphorus is rendered citrate-soluble. The products of the above experiments are known to have given as good results as superphosphate in pot culture trials on neutral or acid soils.

In a private communication to one of the authors, Dr. Harry A. Curtis, of T.V.A. fame, and now Dean of the College of Engineering of the University of Missouri, Columbia, as late as September, 1944, remarked: “Very little has as yet been published on the T.V.A. development in the production of defluorinated tricalcium phosphate. Early in the research programme I published with Copson, Brown and Pole an article giving an account of the work to that date. This article you will find in *Industrial and Engineering Chemistry*, Vol. 29, page 766 (July, 1937). The purpose of defluorination, so far as the production of a phosphatic fertiliser is concerned, is to remove the fluorine from the fluorapatite (sometimes called fluorophosphate), which carries the phosphorus in the natural rock. The phosphorus in natural rock is only slightly available to growing plants, due, presumably, to the fact that calcium fluorophosphate is an extremely insoluble compound. The empirical formula best expressing the chemical composition of calcium fluorophosphate is $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$. Any process which will decompose this molecule and leave alpha-tricalcium phosphate or monocalcium phosphate, or calcium metaphosphate, will render the phosphorus available to growing plants. In the manufacture of superphosphate most of the fluorine remains in the fertiliser in the form of calcium fluoride. In the production of calcium metaphosphate and of defluorinated tricalcium phosphate, the fluorine is nearly all volatilised. In the case of defluorinated tricalcium phosphate, if the defluorination is sufficiently complete (to less than 0.1 per cent F), the material may be used directly as an animal food.”

At this juncture it is deemed advisable to refer to the diagrammatic layout of the phosphoric acid blast furnace, Fig. 2, and to the diagrammatic layout of the plant for the production of phosphoric acid by the electric furnace process, Fig. 3. The two foregoing processes should be considered in relation to what Dr. Curtis has observed in his letter. The heat treatment of phosphate rock cannot be ignored by the superphosphate manufacturers of this country and the European continent. The illustrations given afford details of the raw materials involved in the manufacture of the equivalent of one ton of 100 per cent H_3PO_4 . The blast furnace process is one obviously calling for economy of heat, so as to reduce the quantity of coke used in the actual blast furnace operation to a minimum. The phosphate rock and binder are briquetted and are introduced with coke and sand to the blast

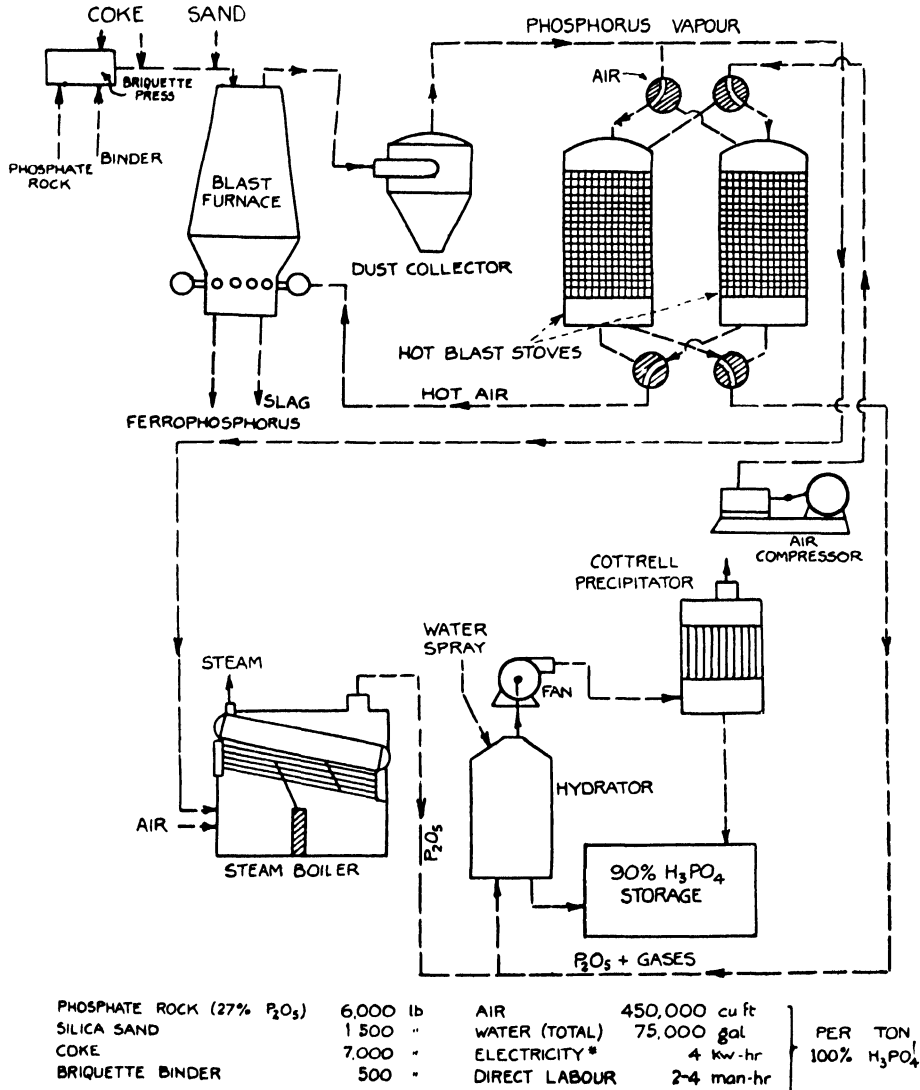


FIG. 2.—PHOSPHORIC ACID BLAST FURNACE PROCESS.

furnace. Ferrophosphate and blast furnace slag are tapped from the blast furnace at predetermined periods. Volatilised phosphorus, associated with dust and steam, etc., is passed through a cyclone for the removal of the dust, and the phosphorus vapour passes to a hot blast furnace stove, packed with refractory brickwork. The introduction of the two hot blast furnace stoves with change-over valves is an important feature of the process, in that considerable heat economy is effected. One of

these stoves is in operation, burning the phosphorus vapour in air, and thus raising the temperature of the refractory brickwork, while air is being passed through the incandescent brickwork of the other stove, which hot air is led to the blast furnace. Thus, apart from the phosphorus being burnt in the stoves in question the heat produced by the combustion of the phosphorus is conserved in this way.

Part of the phosphorus vapour is burnt with air under a steam boiler, and steam is recovered along with the P_2O_5 from the stove in a hydrator tower, which is irrigated with water in the form of an atomised spray. In order to ensure complete recovery of the phosphoric acid, the mist from the hydrator is passed through a Cottrell precipitator, and such precipitated mist is led to the 90 per cent phosphoric acid tank.

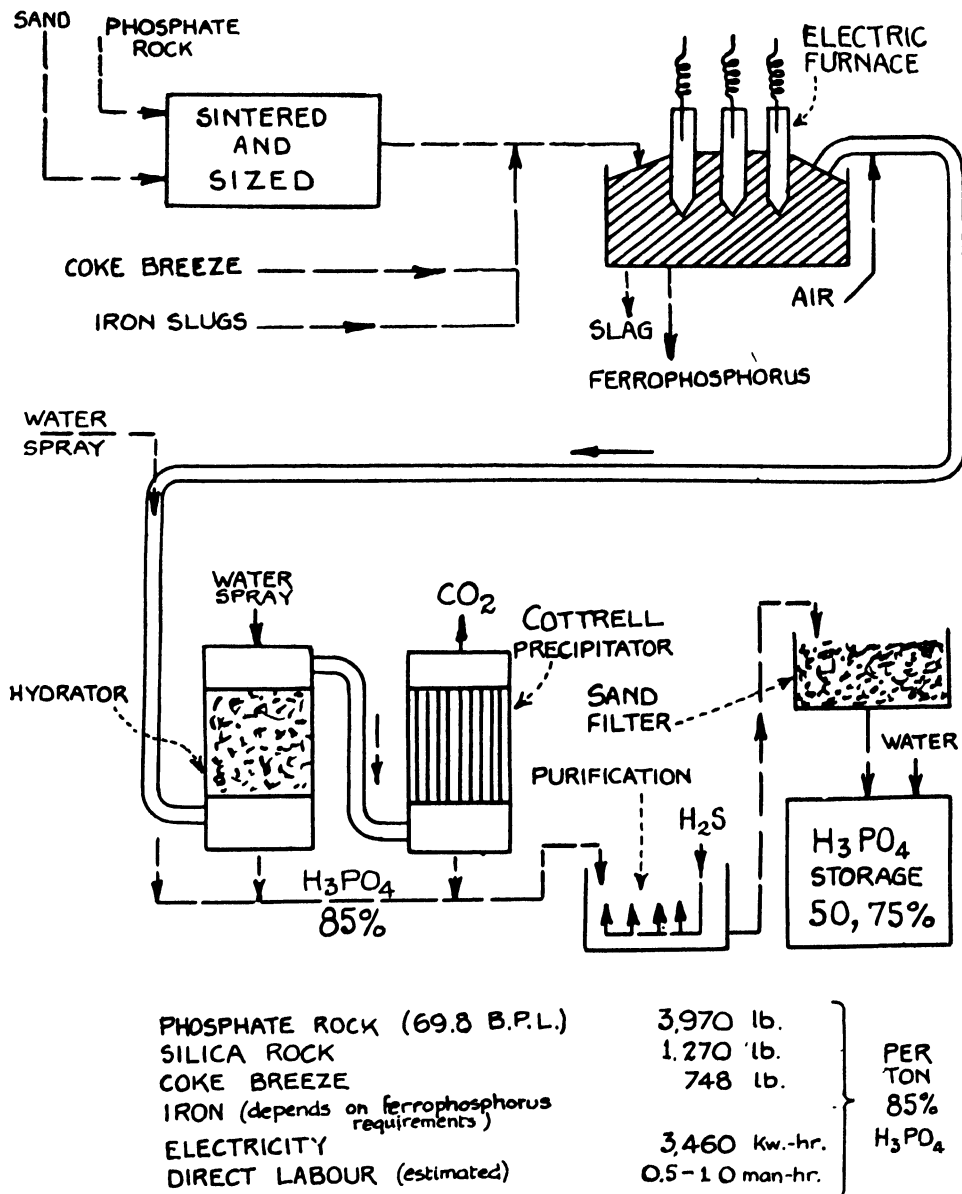


FIG. 3.—PHOSPHORIC ACID ELECTRIC FURNACE PROCESS.

The production of phosphoric acid in the manner just described offers certain advantages over the sulphuric acid method: (1) low-grade ores, which are unsuitable for treatment by sulphuric acid, can be used; (2) the process of washing and screening to separate the phosphate from the gangue can

be simplified; (3) sulphuric acid is dispensed with and (4) there is always the possibility of arranging the blast furnaces at the phosphate mine, thus reducing handling charges and freight.

As regards the electric furnace process, it is believed that there are eight works operating this method in the United States of America at present. The phosphate used at the electric furnace is first sintered in a retort kiln in which pulverised fuel is used. The fine phosphate particles, at a temperature ranging between 1,300 and 1,360° C., are sintered, forming a sinter which is suitable for admission to the blast furnace. The phosphate rock sinter, dry coke breeze and silica rock and iron, are introduced to the electric furnace. P_2O_5 is volatilised and passes to a hydrator and the phosphoric acid, 85 per cent, in turn is purified and thence led to storage tanks. Molten slag—ferrophosphorus mixture—is withdrawn at the bottom of the furnace into a dished open pan, into which the heavier phosphorus deposits. The lighter slag overflows and is granulated into a sand-like product by the application of a stream of water applied at high velocity. Grinding is unnecessary. The slag containing calcium and 1 to 2 per cent P_2O_5 can be used on the land as a material for correcting soil acidity.

The ferrophosphorus is drawn from a lower tap-hole, as is seen in the diagrammatic drawing, into iron moulds, to give a bar-like form. Its composition is about one-fourth phosphorus and three-fourths iron. This material is used in the steel industry.

Whether manufacturers in this country should aim at a defluorinated phosphate, or a silico-phosphate, the production and application of which are receiving the most earnest consideration at the present time, remains to be seen. Economics must obviously play an important part, and the possibility of using these products in lieu of superphosphate, with potash and ammonium sulphate, is a matter calling for the closest investigation. ¹

Silico-Phosphate—Its Constitution and Properties

What is silico-phosphate? Silico-phosphate, concerning which the Ministry of Agriculture and Fisheries issued as recently as 14th March, 1945, circular S.D.B.700, (of which a copy is given as an addendum to this chapter), is not dissimilar to Rhenania phosphate. Chemically, it can be regarded as a sodium silico-phosphate. It is a mixture in solid solution, of two molecules, namely, calcium sodium phosphate and calcium silico-phosphate. It will be recalled that Rhenania phosphate was produced in Germany during the 1914-1918 war, when Germany's own low-grade deposits of phosphate were used. Later, African phosphates were treated, with the addition of sand and soda ash, in a rotary furnace, and a product containing 25 to 28 per cent P_2O_5 was produced, the major portion of which was soluble in a standard solution of citrate of ammonia.

It is understood that A.P.C.M. Ltd., Stroud, are to undertake the manufacture of silico-phosphate on behalf of the Ministry of Agriculture and Fisheries, using existing tube mills and cement kilns for the manufacture. Rock phosphate, with sand, lime, steam and soda ash, are to be used in the manufacture of a product to contain 33 per cent P_2O_5 , which, it should be noted, is twice as concentrated as calcium superphosphate.

Here the question arises: when the process in question is fully developed and established, will soda ash displace sulphuric acid, or is it the intention merely to supplement the supplies of basic slag with silico-phosphate. The possibilities are immense, but it is felt that economic considerations will ultimately be the deciding factor.

The other possibility which looms ahead is the possible establishment of works in this country for the treatment of muriate of potash by sulphuric acid, in the production of sulphate of potash, which has merit as a component of N.P.K. granular fertilisers, as contrasted with muriate of potash. The hydrochloric acid generated would enable another process, which has been developed in the United States, and which is full of promise, to be tried on a practical scale. What is referred to is the new concentrated phosphatic fertiliser, monocalcium chlorophosphate. This material, which has been assigned the formula $CaCl.H_2PO_4.H_2O$, contains about 35 per cent of P_2O_5 , of which 98 per cent is citrate-soluble. This product is prepared by treating phosphate rock with hydrochloric acid of density 1.16, and subsequently with 35 per cent phosphoric acid, thus avoiding the formation of significant amounts of free calcium chloride in the product. Although the chlorine content of the new material is relatively high, field trials have shown it to be without undesirable side effects, and to possess a fertiliser value commensurate with its P_2O_5 content.

Silico-superphosphate, or serpentine-superphosphate, is the name given to material produced by mixing one part of serpentine with three parts of newly-made superphosphate. The magnesium and silica contents of the serpentine are said to be in more active form in the mixture than in the original

rock: in fact, it is claimed that the active silica assists plant growth. In addition to supplying both phosphorus and magnesium to the soil, important trace elements, often lacking in cultivated soils, are also supplied by the mixture. The cobalt content of the serpentine-superphosphate is particularly important in New Zealand, where the material is now being used in part to replace the ordinary type of superphosphate.

Howardists: Humus and Ley Farming

Immersed, as the industry is bound to be, in the problems which have been outlined above, it must not overlook the recent attack of the Howardists, and it must never cease to urge the necessity for ley farming, if humus is to be obtained for the soil. The following oracular utterance of John B. Abbott, of Vermont, should never be disregarded:

“If all the accumulated soil-management wisdom of a hundred generations of master farmers were boiled down to just three sentences, one of these sentences certainly would be: provide for regular and frequent replenishment of the supply of organic matter in the soil.”

Fertiliser salesmen should be taught that humus is not indestructible. When it has become depleted, commercial fertilisers become less effective. This is a common farm experience. Soil fertility can never be stabilised and maintained unless soil humus is retained at a level normal for the origin and for the particular type of soil. Fertilisers, lime and organic matter are undoubtedly complementary: each has a specific role to discharge. But it is the co-operative, or combining, effort that will lead to the big harvest.

On the subject of getting humus to the soil, Sir George Stapledon has been telling us for years how this should be done. Sir George has defined ley farming as the system which takes the plough around practically the whole of the farm, and is conducted in terms of a rotation, or of rotations, based on the use of the ley of a duration of two years or upwards. The need for both lime and phosphates is fully recognised. Sir George has said that no field in permanent grass is too good to be ploughed. A rapid way of creating humus is to arrange a seed-crop, say clover and rye grass. This should be sown in all white straw crops, including wheat, in the spring, and if it is not maintained as a ley, it should be ploughed up after the corn harvest, in order to augment both humus and natural nitrification. Humus constitutes an excellent habitat for micro-organisms, and apart from this, its capacity for retaining moisture—a most valuable property—is said to be eight times that of sand and four times that of clay. The Howardists attach considerable value to the activity of earthworms in promoting soil fertility and in providing nitrogen. But how these insects can be controlled, having regard to their specific functions, is not easy to define.

Trace Elements and Their Value

Another matter to which fertiliser manufacturers should give careful attention is the incorporation in their N.P.K. fertilisers, and indeed in their calcium superphosphate, of trace elements, of which the following are important: calcium, carbon, hydrogen, oxygen, magnesium, iron, sulphur, manganese, boron, copper, cobalt and zinc. Apart from crops removing the three principal elements, calcium is withdrawn in larger quantity than any of the other eleven minor, or trace, elements. Carbon, hydrogen and oxygen are obtained by plants from air and water. With continued cropping it has become apparent that certain soils are deficient in one or more of the remaining eight elements.

Current practice should provide for the addition of relatively small amounts of the deficient elements.

Many symptoms¹ in growing crops that had been considered due to some disease or fungal growth were found to be caused by the lack of one of the minor elements. Magnesium deficiency causes the condition known as “sand drown” in tobacco: manganese deficiency causes chlorosis in tomatoes and other crops: boron deficiency causes “black heart” in mangels and sugar beet, and cracked stem in celery, while zinc deficiency causes “mottle leaf” of citrus trees.

It is still felt that the calcium superphosphate industry in this country should have linked itself with the gas industry long ago, as the latter has been in a position to provide sulphur in the form of spent oxide and by-product ammonia, and mutual advantage would have resulted from a consolidation

¹ *Encyclopaedia Britannica Book of the Year*, 1938, p. 252.

of interests. A great advance has been made in the production of concentrated gas liquor at relatively low costs. Concentrated gas liquor containing 18 to 22 per cent of ammonia by weight can be produced to-day by the Parrish processes (there are five different types of plant available under the name of the "Thorncliffe-Baldurie" system), at about 1s. to 1s. 3d. per unit of ammonia, and even cheaper if steam from waste heat boilers is available at low cost.

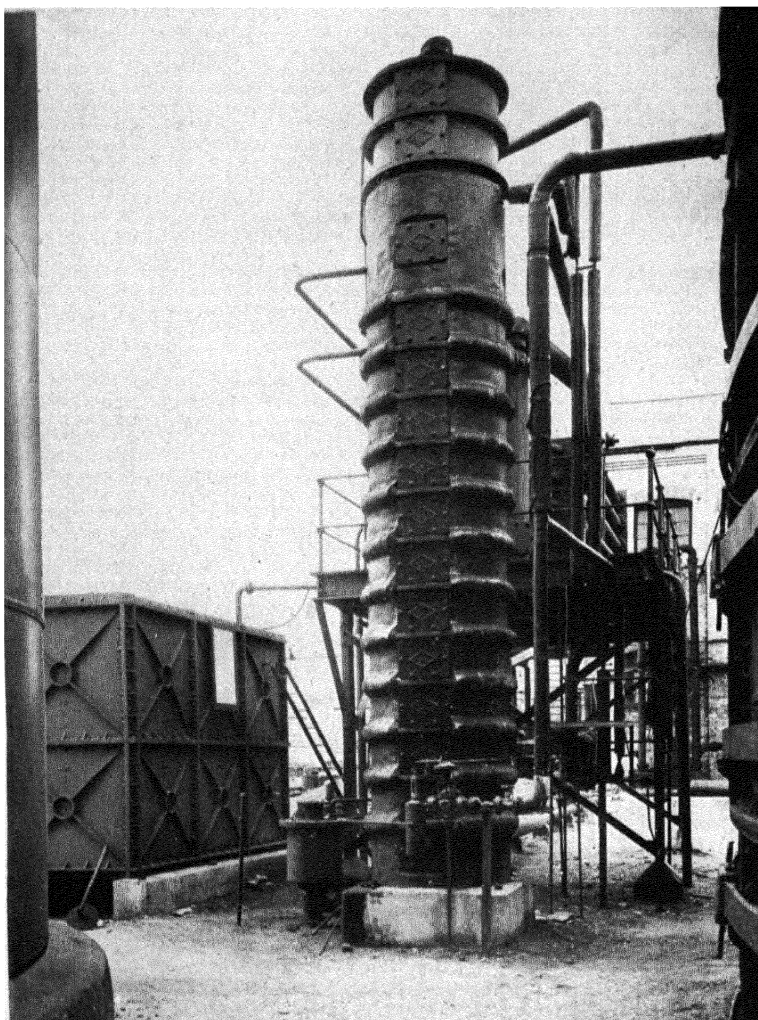


Fig. 4.—CONCENTRATED GAS LIQUOR PLANT—THORNCLIFFE-BALDURIE SYSTEM.

In this country, as indeed in the United States, the war had led the fertiliser industry to establish standard grades for mixed fertilisers. In point of fact, America invoked spokesmen and representatives of the industry to speak in all parts of the States. As a result, recommendations were drafted relating to the most desirable grades for mixed fertilisers for each area. The results were considered officially, and a set of "grade standards" was established. This has led to a substantial economy, because there are fewer grades to be marketed in any given area.

"National Growmore" fertiliser was introduced in this country late in 1942, based on 7 per cent nitrogen, phosphate (P_2O_5) and potash (K_2O), and has been adopted with enthusiasm. The I.C.I.

namely, semi-water gas manufacture, hydrogen conversion, gas compression, gas purification, ammonia synthesis and ammonia storage. Graded coke (with fines removed) is fed to the semi-water gas generators. These supply the nitrogen in the blow-run gas. Water-gas and blow-run gas are mixed and scrubbed with water. Sulphur is subsequently removed and the gas is passed to a storage holder. Additional hydrogen is produced catalytically by the action of the carbon monoxide of the mixture with steam. Synchronous motor-driven compressors withdraw the gas from the converted gas-holder and deliver it through six stages of compression for purification and synthesis. Water-scrubbing at 17 atm. removes CO_2 and carbon monoxide, oxygen and residual carbon dioxide are eliminated by scrubbing the gases with cold ammoniacal copper formate solution at 121 atm. At 350 atm, the final compression is effected. Circulating gas, from which suspended impurities, etc., are filtered out, and the purified synthesis gas are then mixed and the combined volume of new and recirculated gases undergoes refrigeration in an ammonia-cooled condenser. The ammonia-freed gas now passes to a separator, then *via* a heater to the ammonia synthesis converter, the gases emerging from which proceed to a water-cooled condenser. Now the ammonia is removed, which is condensed, and the remaining gases pass into the recirculating system by way of the circulator-compressors. The separated liquid anhydrous ammonia passes through a pressure reduction valve into elevated tanks, where it can be weighed and delivered to spherical tanks for conversion to nitric acid or for the manufacture of ammonium nitrate or other ammonium compounds.

International Phosphate Rock Problem.—The Florida and Tennessee phosphate rock mines have experienced a demand during the last two or three years unprecedented in their experience: indeed, it cannot be doubted that the production of calcium superphosphate in the United States has been arrested to some extent by the absence of phosphate rock on some occasions, and by a dearth of sulphuric acid supplies on other occasions.

The American producers of phosphate rock have viewed with some concern the possibility of most European fertiliser manufacturers taking delivery of their requirements of phosphate rock from North Africa. The large demand for phosphate rock in the United States has caused certain officials in Tennessee misgiving, lest the supply should become exhausted prematurely. But it would appear that there is little fear of a shortage of phosphate rock, although it may be necessary to develop deposits in Montana, Idaho and the adjacent areas. One factor that may retard this development is the greater cost for transport of the rock from remote points to the hub of fertiliser use. How rapidly these deposits are developed depends largely on whether North Africa is likely to be able to satisfy the European demand.

Phosphate Prospects in the United States —The supply of phosphate in 1945 will be governed by the availability of supplies of sulphuric acid. It is believed that 6.5 million tons of superphosphate, based on 18 per cent P_2O_5 , will be required. There is reason to believe that the major portion of the superphosphate will have a concentration ranging from about 18 to 20 per cent of available phosphoric acid. Certainly, less than 5 per cent of the total production will be in the form of concentrated superphosphate, of which the content is invariably 45 per cent P_2O_5 .

International Potash.—The following table gives deliveries of agricultural potash salts of American origin for the twelve months ended May, 1944:—

TABLE 5¹

	Tons K_2O .		
	U.S.	Export, ²	Total.
60 p.c. muriate	434,012	50,359	484,371
50 p.c. muriate	51,444	2,487	53,931
Manure salts	60,064	3,643	63,707
Sulphates	47,824	5,033	52,857
Total	593,346	61,523	654,869

¹ The American Potash Institute.² To Canada, Cuba, Porto Rico and Hawaii.

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Table No. 6 gives the most up-to-date figures available from America, and these are evidence of the growth of the fertiliser industry in that country.

TABLE 6 ¹

Chemical and basis.	Unit.	December, 1944.	December, 1943.	Twelve-month totals.	
				1944.	1943.
Ammonia, synthetic anhydrous (100% NH ₃) ²	Tons	50,833	48,657	543,398	542,879
Nitric acid (100% HNO ₃)	„	41,328	39,571	469,335	485,274
Phosphoric acid (50% H ₂ PO ₄)	„	58,364	53,705	691,954	636,676
Soda ash (commercial sodium carbonate): Ammonia-soda process (98-100% Na ₂ CO ₃): Total wet and dry ³	„	368,588	392,633	4,538,498	4,407,618
Finished light ⁴	„	197,315	205,637	2,455,368	2,299,776
Finished dense	„	124,091	124,515	1,461,832	1,393,952
Sodium hydroxide, liquid (100% NaOH) : ⁵ Electrolytic process	„	103,708	105,482	1,205,039	1,036,577
Lime-soda process	„	62,354	56,037	688,565	663,495
Sulphuric acid (100% H ₂ SO ₄) : ⁶ Chamber process	„	293,503	294,067	3,240,642	3,147,590
Contact process ⁷	„	559,751	523,671	6,028,184	5,456,986
Nett contact process ⁸	„	483,328	459,856	5,311,681	4,888,490

¹ *Chemical and Metallurgical Engineering*, Vol. 52, No. 2.

² Includes a small amount of aqua ammonia.

³ Total wet and dry production including quantities diverted for manufacture of caustic soda and sodium bicarbonate and quantities processed to finished light and finished dense soda ash.

⁴ Not including quantities converted to finished dense soda ash.

⁵ Includes quantities evaporated to solid.

⁶ Collected in co-operation with Bureau of Mines.

⁷ Includes oleum grades.

⁸ Excludes spent acid.

Whether domestic producers of potash continue to expand productive facilities in California and New Mexico remains to be seen. Much depends in the post-war period on governmental policy with respect to potash imports. It cannot be doubted that there are several areas where potash can be produced and shipped to the United States at reasonable prices. It is felt that long-term plans for potash will be largely determined by political considerations, and that the Soviet, Polish, Spanish and British-controlled Palestine operations, which will doubtless be seeking new outlets, may well supply the United States with some of their requirements, if only for the reason that it may be desirable to develop international and reciprocal trade.

Silico-Phosphate—Addendum

Silico-phosphate has a complex composition, and is somewhat akin to the phosphate in the best kinds of basic slag. It is, however, much more concentrated than the highest grades of slag or ordinary superphosphate, though less concentrated than triple superphosphate. It contains about 33% phosphoric acid (P_2O_5) and 1 cwt. of silico-phosphate is therefore equivalent to 2 cwts. of the ordinary pre-war grade of superphosphate.

The phosphate is present in a complex form which breaks down very rapidly in the soil to liberate soluble phosphate, which behaves in the soil in much the same way as the water-soluble phosphate in superphosphate.

Although silico-phosphate is new to this country, a similar material has been used on the Continent since the 1914-1918 war and has held its own against the older forms of phosphatic fertilisers.

The relative values of silico-phosphate, superphosphate and Bessemer basic slag have been tested during the last three seasons in a number of replicated experiments, mostly on root crops and reseeded on phosphate-deficient soils. The dressings were adjusted to supply equal amounts of total phosphoric acid.

In 38 experiments on swedes, silico-phosphate gave 8.0 tons of extra crop as compared with 7.8 tons from superphosphate. In 20 of these experiments Bessemer basic slag was also tested and gave slightly poorer results than the silico-phosphate. On the more acid soils the crops took up 25 per cent more phosphoric acid from silico-phosphate than from superphosphate, probably because the water-soluble phosphate was rapidly locked up in the soil.

In 33 experiments on potatoes silico-phosphate gave 2.5 tons of extra crop as compared with 2.8 tons from superphosphate. For establishment of grass in 23 reseeded experiments silico-phosphate, superphosphate and Bessemer basic slag gave almost identical results. Silico-phosphate also gave excellent results on sugar beet. It has not been tested so fully on other crops, but it may be expected to be at least as good as Bessemer basic slag for autumn-sown cereals.

Silico-phosphate is particularly suited for root crops and reseeded on phosphate-deficient soils. As it is nearly three times as strong as the average grade of basic slag, only light dressings are needed. This makes it economical of labour particularly on rough land and land difficult of access. Suitable dressings to cover the standard rates under the 1944-45 Fertiliser Distribution Scheme for ordinary land and for phosphate-deficient soils are given below.

	Cwts. silico-phosphate per acre.	
	Ordinary land.	Phosphate-deficient soils.
Swedes and potatoes . . .	2	3
Other roots and seeds for three-year leys	1½	2½
Cereals	—	1
Approved dairy pastures .	—	2

N.B.—It should be noted that the Ministry of Supply (Fertiliser Control), has fixed the price of silico-phosphate, 33 per cent P_2O_5 , at £9 6s. per ton, less the usual rebates for early delivery.

CHAPTER II

WORLD'S PHOSPHATE SUPPLY

PHOSPHATE rock is a sedimentary deposit containing tricalcium phosphate of lime. It occurs as a hard rock interstratified with beds of sandstone, shale, or other sediments; as amorphous nodular concretions or pebbles in stream deposits; and as residuum from the decomposition of phosphatic dolomite or limestone, or other rocks containing phosphate of lime.

Another type of deposit commonly classed as phosphate rock is the porous coralline or other limestone of tropical islands, which has been permeated with phosphate leached from guano. Phosphate deposits of the Western United States and North Africa are beds of the first type. Amorphous nodular deposits occur in South Carolina and part of Florida in the United States, in England, Belgium, North-Central and Eastern France, and Russia. The deposits in Tennessee, Kentucky, and some of those in Florida are residual.

Leached guano deposits are found in the Pacific and West Indian Islands.

On account of a diminution in virgin soil fertility throughout the world, the human race is using up the available phosphate supply at an increasing rate. Fortunately, the discovery and opening up of new deposits have so far helped to keep pace with the increased demand, so that there does not seem to be any danger for some time to come of a phosphate shortage threatening the agricultural world.

In 1936 the total output of phosphate rock for the whole world was 11,346,494 tons, representing 3,678,128 tons of P_2O_5 . Of this total America supplied approximately one-third.

The table on page 28 reveals the sources from which the balance of the phosphate rock was derived. There has been a steady increase in the output of phosphate rock over a long period of years.

For instance, in 1907 the world's output was 4,780,000 tons. In 1913 it had increased to 7,230,000 tons, an increase of approximately 50 per cent.

From 1913 until 1936 there has been a further increase of approximately 57 per cent.

In recent years Russia has entered this field of industrial activity, and in 1936 contributed over two million tons towards the world's total output, equivalent to approximately 20 per cent.

Next to the United States, she is the second highest producer.

The Russian phosphate, known as Kola, has not met with much favour in the United Kingdom, chiefly because existing plants are not designed to suit its peculiarities. It is shipped in powder form and requires no grinding, but on account of its extreme fineness it is difficult to unload from ships into trucks, and cases have occurred where workmen have refused to handle it on account of the dust.

A. Wassiliew,¹ writing about Khibina apatite (i.e. Kola phosphate and concentrate), has pointed out that an apatite has a general formula of $Ca_5F(PO_4)_3$, as against the phosphate ore of $Ca_3(PO_4)_2$. Apparently the apatite production of the Khibina deposit has two main branches—apatite rock and apatite concentrates (Kola phosphate concentrate). The former is used largely in the metallurgical industry, and the latter is employed in the production of superphosphate, phosphoric acid, thermophosphates, and other fertilisers and chemicals.

Although it is urged that apatite concentrate is now generally recognised as one of the most suitable products for superphosphate manufacture, due to its extremely high content of tricalcium phosphate, it is known that Kola phosphate concentrate is difficult to handle, by reason of its extreme fineness, and what is more, it reacts very slowly, even when using excess sulphuric acid. The time contact for reaction is appreciably greater than when using Moroccan, Egyptian, Tunisian or U.S.A. phosphate rocks.

Moreover, the fluorine content is never adequately decomposed, and the condition of the superphosphate can hardly be attractive, even when one has resorted to neutralisation of the excess sulphuric acid, which is necessary if the superphosphate is to be sold within reasonable time of manufacture. A special technique must be developed for the utilisation of Kola phosphate concentrate, and it would appear that the U.S.S.R. Industrial Export Corporation (Soyuspromexport) has not yet appreciated how insistent this need is. To-day it is not enough to say that a new product is as satisfactory as

¹ *Fertiliser, Feeding Stuffs and Farm Supplies Journal*, June 17th, 1936, p. 361.

one of established usage: it is essential to demonstrate clearly the technique that will enable a new raw material to yield as satisfactory a final product as that obtained by the use of phosphate rock, and simultaneously to establish its economic advantages.

To overcome the initial difficulty, ships must be unloaded, as is the case with grain, by pneumatic means. Few factories in this country are so situated as to admit of the employment of this method.

Russian Kola phosphate is quarried and is found in three grades. The highest grade contains 28 per cent P_2O_5 , the intermediate and more favoured grade contains 23-25 per cent P_2O_5 , and the poorest grade drops down to 12-15 per cent P_2O_5 .

It is crushed and submitted to an enriching process by means of flotation, which brings the P_2O_5 content up to 37.8 to 39.5 per cent.

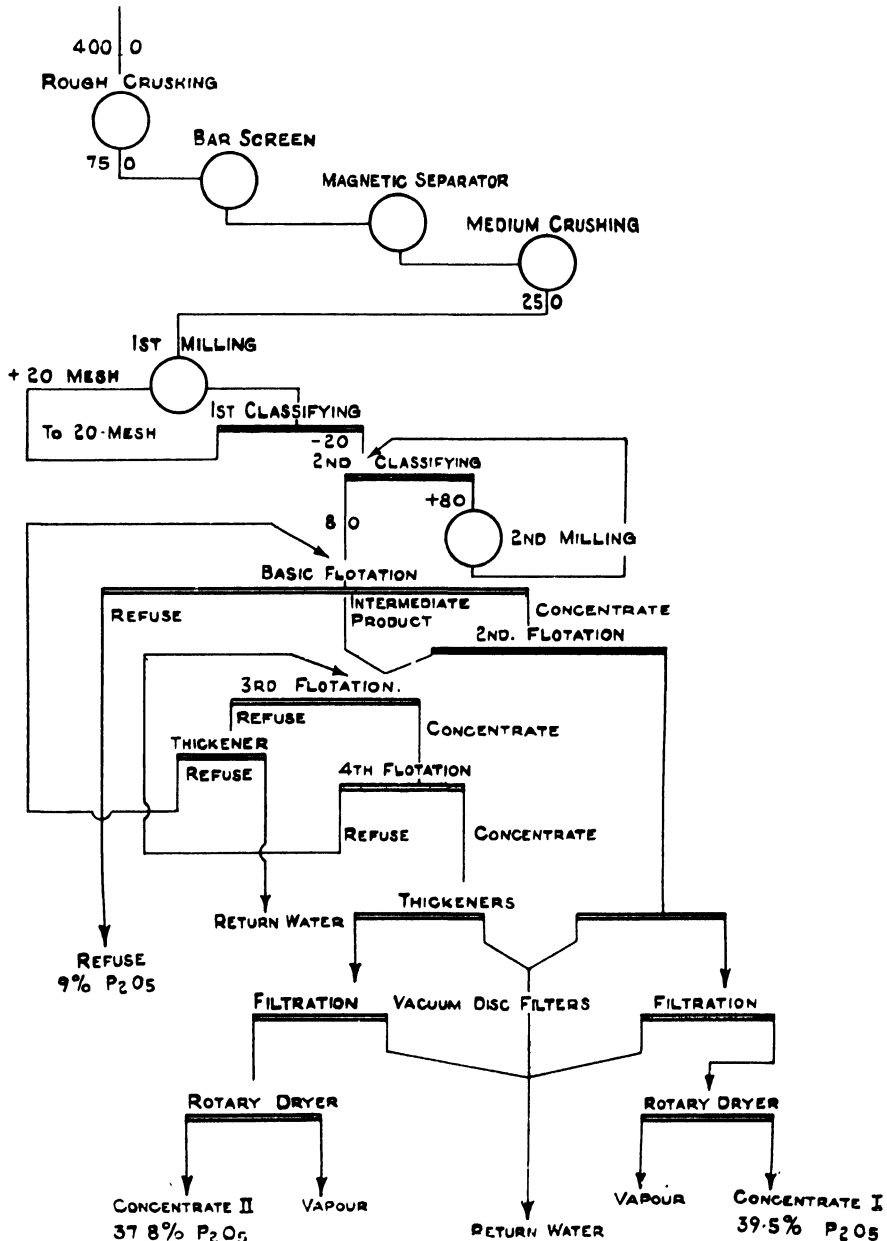


FIG. 6.—FLOW-SHEET OF PROCESS FOR REFINING KOLA PHOSPHATE.

The diagram Fig. 6 is a flow-sheet of the process now employed, which has been in use since 1931.

Referring to the United States, approximately 95 per cent of the output is drawn from Florida and Tennessee. The Florida peninsula contains phosphatic deposits of great magnitude; the area of the field is approximately 1,200 square miles.

In Florida there are two principal categories—Florida “hard rock,” which contains on an average 77.8 per cent tricalcium phosphate; and Florida “land pebble,” which is sold with percentages ranging from 66 to 79.

Florida “hard rock” is hard and compact with a fine homogeneous grain, and is pale yellow in colour. The deposits vary from 5 to 50 feet in thickness. By comparison with North African phosphates it has a lower percentage of carbonate of lime, but it has a higher content of silica.

The following is the analysis of a good sample of hard rock:—

Tricalcium phosphate of lime	83.14 per cent
P ₂ O ₅ content	38.07 ”
Carbonate of lime	3.63 ”
Oxide of iron	2.26 ”
Oxide of alumina	1.52 ”
Silica	4.13 ”
Calcium fluoride	4.4 ”
Water	0.92 ”

Tennessee contains two varieties of phosphate known as “Blue Tennessee” and “Brown Tennessee,” with percentages varying from 65 to 78.

In Africa the Tunisian deposits are of great importance, and in 1936 supplied approximately one and a half million tons towards the world's total.

Tunisian phosphate averages 57 to 65 per cent tricalcium phosphate of lime, and steps have been taken in recent years to enrich it, and plants have been installed for this purpose. It is extremely soft, and when shipped approximately 50 per cent of the bulk passes a 60-mesh British Standard Sieve. This portion is usually separated out and the remainder passed to the grinding mill.

During the period 1914-18, when, owing to the war, more distant sources of supply were cut off, the English factories drew practically all their supplies from this field, and the major portion of our imports still comes from there.

The following may be taken as an average analysis of Gafsa phosphate:—

Tricalcium phosphate of lime	59.44 per cent
P ₂ O ₅ content	27.23 ”
Lime	45.12 ”
Carbonate of Lime	11.95 ”
Oxide of Iron and Alumina	1.68 ”
Magnesium50 ”
Loss on ignition	2.99 ”
Water	2.60 ”

In 1921 mining developments began in Morocco and exports from this region have increased rapidly since that time.

These deposits are estimated to contain over one billion tons, and are situated about 60 miles from Casablanca. The beds are from 24 to 130 feet in thickness and the quality is good.

An analysis by Delattre and Maris is given at the top of next page.

Moroccan phosphate contains a large percentage in powder form, and the rest is quite friable, although it presents certain peculiarities in grinding.

Both in Algeria and Egypt beds of high-grade phosphate are being worked, and further enormous supplies, at present unexplored, are known to exist.

Algerian phosphate averages approximately 65 per cent tricalcium phosphate, and in Egypt deposits are worked containing as high as 75 per cent.

Some of the most important phosphate deposits in the world are located on three small islands, namely, Christmas Island in the Indian Ocean and Ocean and Nauru Islands in the Pacific Ocean, near the Equator.

Water and organic matters combined	3.06	per cent
Sulphuric acid	1.89	"
=3.21 sulphate of lime.		
Phosphoric acid	34.22	"
=74.71 tricalcium phosphate of lime.		
Carbonic acid	2.80	"
=6.36 carbonate of lime.		
Silicious matter	2.56	"
Oxide of iron	0.30	"
Alumina	0.41	"
Lime	52.40	"
Magnesia	0.53	"
Fluorine	2.55	"
=5.23 fluoride of calcium.		
Chlorine	0.30	"
	<hr/>	
	100.75	
Deduct oxygen equivalent to fluorine and chlorine .	1.07	"
	<hr/>	
	99.68	"
Not tested	0.32	"
	<hr/>	
	100.00	"
	<hr/> <hr/>	

Two of these islands—Christmas and Ocean—have long been a part of the British Empire. The other—Nauru—belonged to Germany until November, 1914, when it was seized by the British Navy and assigned permanently to the British at the Peace Conference. By the Nauru Island Agreement Act of 1919, the phosphate was to be divided between England, Australia, and New Zealand, in the ratio of 42, 42, and 16 per cent respectively.

These allotments are for home consumption for agricultural purposes in the country of allotment, and not for export. The basis of the allotment is to be readjusted every five years in accordance with the actual requirements of each country. If in any one year one of the three countries does not require its full allotment, the other two countries are entitled, so far as their requirements for home consumption extend, to have the excess assigned to them in the proportions to which they are entitled as above.

So far England has not taken her quota.

The phosphate deposits in these three islands are among the richest of the world's supply. Their percentages of tricalcium phosphate are as follows:—

Christmas Island phosphate	80.00	per cent
Ocean Island phosphate	85.88	"
Nauru Island phosphate	85.89	"

Though Ocean Island phosphate is slightly higher in quality than the Nauru product, the latter lends itself better to the manufacture of superphosphate, and, generally speaking, is preferred by the fertiliser manufacturers on that account.

An analysis of Nauru phosphate is given as follows:—

Tricalcium phosphate of lime	85.89	per cent
P ₂ O ₅ content	39.34	"
Carbonate of lime	4.69	"
Oxide of iron and alumina	0.76	"
Organic matter	2.86	"
Water	3.87	"

TABLE 7

*Phosphate Rock—World Production 1937-1939
In Tons of Product and of Phosphoric Acid ¹*

Country.	1937		1938		1939		Grade.
	Tons Rock	Tons P ₂ O ₅	Tons Rock	Tons P ₂ O ₅	Tons Rock	Tons P ₂ O ₅	
EUROPE :							
Austria	—	—	—	—	—	—	26.00
Belgium	68,356 ¹	14,355	75,000 ⁴	15,750	33,996	7,139	21.00
Estonia	10,112	2,022	13,012	4,034	15,000 ⁴	4,650	31.00 ⁸
France	103,469 ¹²	34,145	82,000 ⁴	27,060	25,410	8,385	33.00
Germany	3,314 ¹²	829	3,221	805	— ⁶	—	25.00
Poland	5,400	918	—	—	10,000	1,700	17.00
Roumania	950	238 ¹⁴	970 ⁸	242	— ⁶	—	—
Russia ¹⁰	2,300,000	690,000	2,350,000	705,000 ⁴	2,137,450	641,235	30.00
Spain	—	—	24,953	7,361	64,000	18,880	29.50
Sweden ¹²	4,916	1,475	6,192	1,858 ⁴	7,500	2,250	30.00
TOTAL	2,496,517	743,982	2,555,348	762,110	2,293,356	684,239	
AFRICA :							
Algeria	631,119	183,656	584,500	170,090 ¹³	593,905	172,826	29.10
Egypt	516,978	155,093	458,400	137,520 ¹³	447,965	134,390	30.00
Morocco	1,378,443	479,009	1,487,000	498,145 ¹³	1,491,754	499,738	33.50 ⁸
S. Africa	—	—	—	— ¹⁴	126	34	27.00
Tanganyika	104	28	106	29 ¹⁵	432	117	27.00
Tunisia	1,771,457	496,008	2,034,200	569,576 ¹⁵	1,827,745	511,769	28.00
TOTAL	4,298,101	1,313,794	4,564,206	1,375,360	4,361,927	1,318,874	
AMERICA :							
Canada	90	34	200	76	142	54	38.00
Chili ²	—	—	24,000	7,200	9,014	2,704	30.00
Curaçao ⁷	98,672	35,188	104,470	37,087	65,081	23,104	35.50 ⁸
U.S.A. ⁹	4,329,599	1,428,768	3,922,244	1,294,341	4,051,778	1,337,141	33.00
TOTAL	4,428,361	1,463,990	4,050,914	1,338,704	4,126,015	1,363,003	
ASIA :							
British India	169	63	23	9	185	68	37.00
China	—	—	— ⁶	—	— ⁶	—	38.00
Dutch E. Indies	26,166	9,158	33,111	11,589	30,000	10,500	35.00
Indo-China	20,249	7,492	37,339	13,815	35,694	13,207	37.00
Japan ¹¹	121,795	45,673	150,390	56,396	233,811	87,679	37.50
TOTAL	168,379	62,386	220,863	81,809	299,690	111,454	
PACIFIC AND INDIAN OCEANS :							
Angaur ⁷	90,652	33,315	105,577	38,800	143,420	52,707	36.75
Australia	20	5	498	124	—	—	25.00
Christmas Island ⁷	165,169	64,416	162,417	63,343	155,569	60,672	39.00
Madagascar ⁷	4,300	1,505	5,691	1,992 ²⁴	6,600	2,310	35.00
Makatea ⁷	158,841	60,360	102,940	39,117	170,627	64,838	38.00
New Caledonia	300	105	5,000	1,750	1,200	420	35.00
Ocean/Nauru	1,105,103	436,516	1,158,849	457,745	1,277,188	504,489	39.50
Philippines	750	270	— ⁶	—	— ⁶	—	36.00
TOTAL	1,525,135	596,492	1,540,972	602,871	1,754,604	685,436	
GRAND TOTAL	12,916,493	4,180,644	12,932,303	4,160,854	12,835,592	4,163,006	
AVERAGE GRADE	32.37%		32.18%		32.43%		

There are said to be no less than 100,000,000 tons of phosphate on the Nauru and Ocean Islands. How these extensive and wonderfully rich deposits came into existence has been the subject of much conjecture. What is known as the "bird" theory is the most popular and generally accepted. The original guano, in the form of bird excreta, must have been deposited many thousands of years ago. There is evidence that the islands have been submerged on several occasions. The result is that all impurities have long since been washed away, and practically only the pure phosphate of lime remains. Curiously enough, the birds believed to be responsible for these deposits are now extinct, and the islands to-day are rarely, if ever, visited by birds.

Other minor deposits occur in Australia, Spain, Belgium, France, Japan, Canada, and Curaçao. Those in Curaçao are of fine quality, resembling closely the hard rock of Florida, but they are not extensive. Phosphate deposits at the foot of the Himalayas, known as Deradun phosphate, have been found and a nodular phosphatic deposit exists in Trichinopoly. Both these deposits are about to be worked. Moreover, in the U.S.S.R. a most extensive and valuable deposit has been found in Kazakhstan, known as the Kara-Tau deposit. This deposit lies near the east of the Caspian Sea in the foot-hills of Tibetan-Himalayas. It is understood that these deposits are to be worked on a formidable scale.

Some recent detail¹ of Kazakhstan should be given, in view of the significant deposit indicated. Its area is 1,037,458 square miles. population (1933), 6,797,000: Kazakhs, 57.1 per cent, Russians, 19.7 per cent and Ukramans, 13.2 per cent. Leading cities (1935 populations), Alma Ata (the capital, formerly Verny), 197,400; Semipalatinsk, 136,000; Karaganda, 118,900. Languages: Kazakh, Russian and Uzbek. Natural resources (estimated): coal, 60 milliard tons; oil, 1,292.2 million tons; copper, 11 million tons, lead, 2.6 million tons, zinc, 4.6 million tons.

It is interesting to note from Table 7 that the European countries draw their phosphate supplies from nearly all the available sources of supply.

¹ *Encyclopaedia Britannica*, 1939, p. 367.

NOTES TO TABLE 7.

¹ Including 52,267 tons Mons phosphate.

² Partly estimated on basis of fertiliser produced.

³ Grade 39.5 per cent prior to 1938.

⁴ Estimated.

⁵ 34.75 per cent (dry basis) prior to 1938; 33.5 (wet basis) present basis of sale.

⁶ Figures not available.

⁷ Exports.

⁸ 20 per cent prior to 1938.

⁹ U.S.A. Bureau of Mines.

¹⁰ Apatite and phosphorite production; estimated.

	Daitojima.	Rasa.	Pelew.	Rota.	Tocobe.	Saipan.	Fais.	Variou.
1937 . . .	35,160	53,917	21,621	9,669	1,428	—	—	—
1938 . . .	24,434	61,248	18,073	29,770	2,773	3,658	10,434	—
1939 . . .	35,277	53,049	26,303	43,539	4,269	20,679	43,821	6,874

¹¹ British Imperial Institute.

¹² Total of mining companies' deliveries.

¹³ Production of S.W. Africa.

¹⁴ Chiefly bat guano.

¹⁵ U.S.A. Bureau of Mines.

¹⁶ *Phosphates and Superphosphate*, by A. N. Gray, p. 255.

CHAPTER III

THE HISTORY AND CHEMISTRY OF THE MANUFACTURE OF SOLUBLE PHOSPHATES

PRIOR to the introduction of calcium superphosphate as a fertiliser, it was known that the action of vitriol on bone ash produced a soluble phosphate of lime. The composition of this product, as indeed of other phosphates, had been the subject of study by Berzelius.

This knowledge appears to have found application to agriculture about the year 1840.

That Liebig was responsible for the suggestion appears certain. In his report to the British Association in 1840 he referred to bones as a manure, urged the importance of fine grinding, and pointed out that by pouring over bones, in a state of fine powder, half of their weight of diluted sulphuric acid, a practical method of obtaining suitable division was ensured.

In May, 1842, a patent for making superphosphate "by decomposing bones, bone ash, bone dust, and other phosphoric substances, mixing a quantity of sulphuric acid just sufficient to set free such phosphoric acid as will hold in solution the undecomposed phosphate of lime," was granted to J. B. Lawes.

This patent reveals a certain knowledge of the chemical changes accompanying the application of sulphuric acid to phosphatic matter.

The claim of Lawes, however, was not allowed to go unchallenged. But on learning of Liebig's published suggestion, Lawes modified his patent, and confined his claim to apatite, phosphorite, and other substances containing phosphoric acid.

To Lawes is due the credit of having at least introduced the mineral superphosphate industry to this country, although Liebig was no doubt the precursor as regards the natural materials—bones, etc.

As is usual with an important discovery, other claimants were soon in the field. Despite the plausibility of their pretensions, the position as previously stated does not appear to have been disturbed.

The calcium superphosphate originally manufactured by Lawes was a mixture of soluble and insoluble phosphates obtained from coprolites or from guanos, mixed with animal matter and ammoniacal salts. It resembled dissolved bones, and was not unlike the product sold to-day as soluble bone compound.

It is said that the material varied somewhat in quality, but an idea of its composition, and the limits within which it varied, are given below.

Nitrogen	3.24 to 0.12 per cent
Soluble phosphate of lime	18.05 to 1.60 „
Insoluble	0.06 to 28.3 „

This analysis is due to Way¹ (1851).

By 1862—twenty years after the granting of the patent to Lawes—the manufacture of superphosphate had increased to between 150,000 and 200,000 tons per annum, whereas in 1907, 700,000 tons were made in the United Kingdom, of which 120,000 tons were exported.

The figure of consumption for Great Britain, Northern Ireland, and Eire for the season 1937-38 was 566,517 tons, as compared with 1,000,000 to 1,200,000 tons, which is the estimated consumption during the season 1945-46. But the indications are that for the ensuing season there will be an increased sale.

But it would be wrong to suppose that an important output such as obtained in 1862 necessarily synchronised with the best type of manufacturing plant, operated under the best conditions. Any such assumption would be unfounded.

In much the same way as other industries have been evolved degree by degree and stage by stage, so the calcium superphosphate industry has advanced. It constitutes no exception to the general rule.

¹ Professor Way, chemist, of the Royal Agricultural Society of England.

About 1860, the plant used in the manufacture of superphosphate was simple, and the methods of operation somewhat crude. The artificial fertiliser factory of those days had buildings (*a*) for the reception of the raw phosphate and (*b*) for the storage of the finished product. A third building was assigned to the actual process. Machinery was largely absent. An acid storage tank and a few measuring tanks constituted the equipment, apart from the dens, which were two or more in number, according to the size of the factory.

It is known that in some cases these (the dens) consisted of pitch-pine joists, 9 inches by 3 inches, well tarred and suitably braced. In other cases brickwork dens were used. These were built by immersing the bricks in hot tar. At other works, in order to prevent warping or unshapeliness of the brickwork, it is known that 1-inch thick cast-iron flanged plates were employed.

The method of operation does not call for any elaborate comment. The requisite quantity of acid, determined originally by trial and error, of 106° – 112° Tw., was run on to a suitably formed heap of fine raw phosphate which had been weighed. The two were incorporated thoroughly by means of rakes, the phosphate being applied to the acid gradually and the mixture turned frequently with the shovel.

The mass soon showed signs of thickening, and at times even set before the incorporation was finished.

To obtain uniformity of product the mass was moved from one side of the den to the other. Later, it was filled into barrows and transferred to the superphosphate storage building. For several months it was allowed to lie there to mature. Finally it was screened by hand and delivered to the customers.

Such were the plant and method of manufacture about the year 1860.

As time elapsed, the quality and physical characteristics of raw phosphate changed. New sources of supply were found and developed. Some of these phosphates were much harder than those hitherto employed. Moreover, there were differences in chemical composition. It was soon evident that, if difficulties in manufacture were to be avoided, special grinding plant would be necessary.

Thus it is found that the more important factories took steps to install French burrs, or roller mills, etc. Crushers were shortly afterwards introduced. About this time the Carr's disintegrator was adopted for crushing the finer product. The results following the use of this machine were not always uniformly satisfactory. This was not due so much to any peculiar disability attaching to the operation of the machine itself as to the absence of uniformity in the physical quality and chemical composition of the superphosphate undergoing mechanical treatment.

Where disintegration was satisfactory it was usual subsequently to employ a conical rotary screen so as to reduce the material to a uniformly fine size. The finer material passed through the screen, the coarser product being retained in the reel and discharged at the end. All the coarse material was returned to the disintegrator for further crushing.

But with the introduction of mechanical plant there came the realisation that the operation of superphosphate manufacture was, after all, something more than the mere admixture of fine raw phosphate with dilute sulphuric acid. Complaints about the product and irregularities in the manufacture confirmed the more intelligent manufacturers in the view that chemical control was at least a necessary adjunct to successful and efficient manufacture.

Apart from the trial-and-error method of determining the details of the mixings, it was slowly being appreciated that the chemical compositions of the various raw phosphates were dissimilar, that the precise strength and temperature of the acid used played a part in the ultimate quality of the manufactured product, as indeed did the duration of mixing and the ease and speed with which the resulting vapours and steam were removed.

The gradual reversion of small quantities of soluble phosphate - a phenomenon which revealed itself about this period (1880)—was also an additional proof of the need for chemical control as distinct from the empirical methods of the past.

It is true that in some factories a chemist was employed, but this was by no means general. His importance, however, became increasingly insistent about this time.

The operation of mixing in the den was superseded by mechanical mixing, with the introduction of apatite from Canada and Norway, and with the supply of mineral phosphates from Florida, etc. The presence of chlorides, and particularly fluorides, in such raw materials, which were released when undergoing decomposition by treatment with sulphuric acid, constituted a menace to the health of the operatives, besides creating a nuisance in the locality of the works.

About 1880 the installation of condensing plant to deal with chlorine and fluorine and other vapours became necessary. Towers of wood or brickwork were built, and these were packed with a

suitable filling medium, boards on edge, or coke, and profusely sprayed with water. The hydrofluosilicic acid was arrested in this way.

To pursue in detail the further developments of the superphosphate industry as regards plant and practice is uncalled for. It will suffice if brief mention is made of the nature of the subsequent stages of development.

With the recognition that fine grinding was essential to the efficient manufacture of calcium superphosphate came the introduction to the fertiliser factories of ball mills, ball mills combined with tube mills, Griffin's pendulum crusher, and ring-roll mills of several types.

Fine grinding involved the necessity for the recovery of the dust, and various forms of dust chambers embodying different principles were adopted.

Similarly, the necessity for economic handling of the raw materials and finished products became more and more apparent. This led to the introduction of various types of transport systems, such as aerial ropeways, steel tray and belt conveyors, bucket elevators, etc.

To secure a dry pulverulent "super" was a problem which engaged attention for some time. One of the methods adopted, particularly following the introduction of Florida phosphate, was to resort to artificial drying. But this process was hardly an unqualified success, as will be surmised from what has already been written. While drying reduced the amount of water in the superphosphate, the percentage of free phosphoric acid, as indeed of hydrofluosilicic acid, increased, and such a product was not without its disabilities. It attracted moisture, and contributed to the destruction of the bags.

But the greatest advance about this time (about 1900) was an appreciation of the fact that the fine subdivision of the superphosphate and a reduction of the free acidity would alone give the desired quality of product.

Mechanical dens with mechanical cutting devices and improved draught appliances have undoubtedly conduced to a material improvement in the physical, mechanical, and chemical properties of superphosphate. This feature, as well as other advances in technique, will be enlarged upon in detail in the subsequent chapters. In introducing each of the unit processes involved in the manufacture of calcium superphosphate further allusion to historical developments will be briefly made.

The Chemistry of Phosphorus Compounds

A few words will be devoted to the chemistry of phosphorus compounds in fertilisers before proceeding to the chemistry of the soluble phosphates.

Phosphatic fertilisers are all substances containing some form of calcium phosphate. The varieties of calcium phosphate are many.

Phosphorus pentoxide (P_2O_5) is the only oxide of phosphorus found in fertilisers, and the only acids which need concern us are those derived from phosphorus pentoxide. No pentahydrate of phosphorus, such as one would be entitled to suspect, exists, although all the phosphorus compounds are found in dehydrated forms of it.

There are three phosphoric acids, resulting, as has been tacitly indicated, by combination of phosphorus pentoxide with one, two, or three molecules of water. These are known respectively as:

- (a) Metaphosphoric acid. $P_2O_5 \cdot H_2O$, HPO_3 , being $\frac{1}{2}(P_2O_5 \cdot H_2O)$.
- (b) Pyrophosphoric acid. $P_2O_5 \cdot 2H_2O$, or $H_4P_2O_7$.
- (c) Orthophosphoric acid. $P_2O_5 \cdot 3H_2O$, or H_3PO_4 .

Orthophosphoric acid is the most commonly-occurring. Pyrophosphoric acid only occurs in substances which have been subjected to heat. Metaphosphoric acid is a product of overheating.

The two last named—pyro- and meta-phosphoric acids—are both converted into orthophosphoric acid on boiling in acid solutions. Similarly, in the presence of excess water, even if the solutions are cold and neutral or alkaline, such a change as that already indicated occurs, but the reaction, as will be suspected, is a very slow one.

It is possible to discriminate between the three phosphoric acids named without much difficulty.

Metaphosphoric acid gives a white precipitate, both with barium chloride and silver nitrate, and it coagulates a solution of albumen. Pyrophosphoric acid gives no precipitate with barium chloride,

but a white precipitate with silver nitrate, and it does not possess the power of coagulating albumen ; orthophosphoric acid gives no precipitate with barium chloride, but a yellow precipitate with silver nitrate, and does not coagulate albumen.

The calcium salts of orthophosphoric acid are found in all phosphatic fertilisers, and consist of :

- (a) Monocalcium phosphate, which may be represented thus : $\text{CaH}_4(\text{PO}_4)_2$;
- (b) Dicalcium phosphate, represented thus : $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$; and
- (c) Tricalcium phosphate, represented by the formula $\text{Ca}_3\text{P}_2\text{O}_8$.

All three calcium orthophosphates are unstable in water, breaking down, as they do, into solids containing more lime than the original solid. In solution, the ratio of acid to lime is greater than in the original solid.

F. K. Cameron, A. Seidell, and J. M. Bell have investigated the composition of the aqueous solution containing calcium hydroxide and phosphoric acid. A significant part of their results will be found in Tables 8, 9, and 10, illustrating as they do the solubility of the solid phases at temperatures of 25°C ., 40°C ., and 50.7°C . A study of these results will prove peculiarly instructive.

Conditions of equilibrium of the calcium orthophosphates in aqueous solutions of phosphoric acid

TABLE 8

25° C.		
Grm. per 100 gm of saturated solution.		Solid Phases.
CaO.	P ₂ O ₅ .	
3.088	36.11	Ca(H ₂ PO ₄) ₂ H ₂ O.
4.908	28.34	
5.809	24.20	Ca(H ₂ PO ₄) ₂ H ₂ O : CaHPO ₄ .
5.523	22.90	CaHPO ₄ .
4.990	17.55	"
2.638	9.100	"
1.878	6.049	"
0.826	2.387	"
0.165	0.417	CaHPO ₄ : CaHPO ₄ 2H ₂ O.
0.070	0.166	CaHPO ₄ 2H ₂ O.
0.060	0.140	"
0.050	0.118	"
0.040	0.093	"
0.030	0.070) More basic than CaHPO ₄ 2H ₂ O.
0.020	0.047	
0.010	0.023	

TABLE 9

40° C.		
Grm. per 100 grm. of saturated solution.		Solid Phases.
CaO.	P ₂ O ₅ .	
1.768	42.42	Ca(H ₂ PO ₄) ₂ H ₂ O.
3.584	36.79	
5.755	27.25	Ca(H ₂ PO ₄) ₂ H ₂ O : CaHPO ₄ .
4.813	21.67	CaHPO ₄ .
3.810	16.35	"
2.536	9.905	"
1.847	6.979	"
1.267	4.397	"
0.576	1.819	"
0.156	0.426	"
0.0592	0.158	"
0.0508	0.128	Ca ₃ (PO ₄) ₂ H ₂ O.
0.0098	0.0262	"

TABLE 10

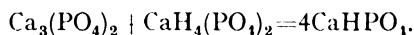
50.7° C.		
Grm. per 100 grm. of saturated solution.		Solid Phases.
CaO.	P ₂ O ₅ .	
0.336	62.01	Ca(H ₂ PO ₄) ₂ : Ca(H ₂ PO ₄) ₂ H ₂ O.
0.635	58.08	Ca(H ₂ PO ₄) ₂ H ₂ O.
1.428	50.25	"
2.974	41.92	"
4.880	33.18	"
5.725	29.61	Ca(H ₂ PO ₄) ₂ H ₂ O : CaHPO ₄ .
3.507	15.48	CaHPO ₄ .
2.328	9.468	"
1.563	6.157	"
0.692	2.281	"
0.0596	0.1527	CaHPO ₄ 2H ₂ O.
0.0514	0.1331	Ca ₃ (PO ₄) ₂ H ₂ O.
0.0351	0.0942	"
0.0106	0.0309	"
0.0007	0.0007	"

*Calcium Orthophosphates*¹

A reasonably pure crystalline product with well-defined characteristics, of a definite molecular species, has not been prepared. What is obtained is a white earthy powder,² which retains water very tenaciously.

The reactions between calcium phosphate and sulphuric acid have been studied by Kolb, Millot, Weber, Piccard, Joulie, Crun, Armsby, and Erlenmeyer. If one to two molecules of sulphuric acid are used for a molecule of normal calcium phosphate ($\text{Ca}_3\text{P}_2\text{O}_8$), and enough is added to make the whole into a "slip," Millot has found that $\text{CaH}_4(\text{PO}_4)_2$ and CaSO_4 are formed. If less than one molecule of sulphuric acid is used, 50 per cent of the calcium phosphate remains unchanged.

Armsby has found that the amount of soluble phosphate— $\text{CaH}_4(\text{PO}_4)_2$ —which is formed by the sulphuric acid depends on the temperature and on the duration of the reaction; and he assumed that $\text{CaH}_4(\text{PO}_4)_2$ is initially formed by the action of the acid, and that this then reacts with the unchanged calcium phosphate to form the dicalcium phosphate, thus:



Millot further showed that with two molecules of sulphuric acid, per molecule of normal phosphate, 69.63 per cent of soluble phosphate is formed, and with equimolecular proportions the soluble phosphate in the product decreases, owing to the formation of CaHPO_4 , while Kolb assumed that free phosphoric acid is formed by the action of two molecules of acid and one molecule of calcium phosphate, which, on standing, forms $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

The apatite group is another class of phosphorus compounds which concerns us. A true apatite can be regarded as a fluorine compound, having the formula $\text{Ca}_5(\text{PO}_4)_3\text{F}$. It is a crystalline substance, found in the enamel of animals' teeth and in minerals.

There are other forms of apatite, such as chloro-apatite, in which fluorine is replaced by chlorine; hydroxy-apatite, in which the fluorine is replaced by the hydroxyl group (OH); as well as organo-apatite, where one finds fluorine substituted by organic matter. An exemplification of the latter is the principal constituent of bones, where some phosphate occurs as a sclero type—the gelatinous matter of bones displacing the fluorine.

Bone phosphates are regarded by some authorities as a carbono-apatite [$\text{Ca}_5(\text{PO}_4)_3\text{C}'\text{O}_3$], and equally there is evidence to support the assumption that the water in soluble nitrogenous matter occurring in milk is a casein apatite.

In some special cases calcium occurs as a basic phosphate, with more calcium in it than tribasic phosphate, and where the acid involved is less dehydrated than orthophosphoric acid.

In addition, there are some silico-phosphates met with in some fertilisers, (*vide* p. 23).

Monocalcium phosphate is stable in the presence of hydrochloric acid. If any of the calcium phosphates are dissolved in hydrochloric acid and evaporated to dryness, it will be found that the monocalcium phosphate remains behind. The same result follows the evaporation of a mixture of phosphoric acid and calcium chloride. It is found that dicalcium phosphate will absorb hydrochloric acid gas when passed over it. Tricalcium phosphate is attacked slightly by carbonic acid, and produces solutions which are said to contain some dicalcium phosphate.

The phosphates of the alkalis are all soluble in water. The phosphates of the alkaline earths are soluble in acetic acid but insoluble in water, whereas ferric and aluminium phosphates are insoluble in acetic acid.

The Chemistry of Soluble Phosphates

Despite the introduction of chemists to the superphosphate industry, to which reference has been made earlier in this chapter, it is doubtful if the scientific control of the processes involved has been on a scale commensurate with the improvements of the plant employed and the growing resources of the raw materials.

It is not easy to assign a reason for this. Various explanations have been offered. A chemically pure product is not the aim of the fertiliser manufacturer when ground rock phosphate is acted upon by sulphuric acid. Rather is it the desire that the product shall possess certain chemical and physical properties. The aim is to secure the maximum proportion of soluble monocalcium phosphate,

¹ Dr. Mellor's *Inorganic Chemistry*.

² Basset, *J. Chem. Soc.*, 111, 620 (1917).

combined with a friable and granular texture, admitting of ready manipulation and mixing, and allowing of suitable use with mechanical distributors. If attention were directed alone to the chemical characteristics of the product, there can be no doubt that the physical attributes of the superphosphate would suffer. The latter features cannot be computed from chemical equations or factors. Trial-and-error methods of mixing in the past seem to have appealed more strongly and directly to fertiliser manufacturers than theoretical deductions.

That theory (known facts, duly marshalled and generalised) can be co-ordinated with practice appears certain, and recently this has been one of the directions in which fertiliser chemists have attempted to make some advance.

The importance of the phase rule in reactions such as are involved in the manufacture of superphosphate has not always been fully appreciated. That the phase rule plays a significant part is not now disputed.

Several workers have investigated the theory of soluble phosphates, and have approached it from the point of view of the phase rule. Cameron and Bell¹ have partially studied the four-component system CaO, H₃PO₄, H₂SO₄, and H₂O, and their findings have been represented by a series of diagrams similar to Fig. 6.

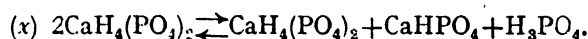
O represents a saturated solution of lime in water. On the Ox axis A represents a solution in equilibrium, with dicalcium phosphate and the limiting solid solution; and B, a solution saturated with both mono- and di-calcium phosphate. On the Oy axis, C represents a solution saturated with both calcium hydroxide and gypsum, and D a solution in equilibrium with both gypsum and anhydrite. The fields over which the calcium phosphate can exist are very narrow. The data for 25° C. are shown in Table 11. The changes which occur by raising the temperature have been partially investigated.

TABLE 11

Fig. Letter.	Grm. P ₂ O ₅ per litre.	Grm. SO ₂ per litre.	Grm. CaO per litre.	Solid Phases.
O	0	0.0	1.17	Ca(OH) ₂ .
A	3	0.0	1.15	Solid sol. CaHPO ₄ ·2H ₂ O.
B	317	0.0	77.00	Ca(H ₂ PO ₄) ₂ ·H ₂ O : CaHPO ₄ ·2H ₂ O.
C	0	0.9	1.90	Ca(OH) ₂ : CaSO ₄ ·2H ₂ O.
D	0	317.5	1.00	CaSO ₄ ·2H ₂ O : CaSO ₄ .
E	3	0.9	1.50	Solid sol. CaSO ₄ ·2H ₂ O : CaHPO ₄ ·2H ₂ O.
F	317	0.6	77.00	CaSO ₄ ·2H ₂ O : CaHPO ₄ ·2H ₂ O : Ca(H ₂ PO ₄) ₂ ·H ₂ O.
G	545	0.2	38.00	CaSO ₄ ·2H ₂ O : CaSO ₄ : Ca(H ₂ PO ₄) ₂ ·H ₂ O.

The point F moves to the right, G to the left. At 66° the two points meet, and there is a sextuple point where the six phases—solution, vapour, CaSO₄, CaSO₄·2H₂O, CaHPO₄·2H₂O, and Ca(H₂PO₄)₂·H₂O—are in equilibrium.

Approaching the matter again from the viewpoint of other investigatory work, and taking initially the chief constituent, calcium phosphate, normally there is a solid phase, consisting of mono- and di-calcium phosphates, and a liquid phase, consisting of phosphoric acid, water, and monocalcium phosphate in the system (to use the parlance of the phase rule) phosphoric acid, calcium oxide, and water. To what extent free phosphoric acid and dicalcium phosphate exist depends in practical working on the water introduced via the sulphuric acid. A unit weight of water at constant temperature will dissolve increasing quantities of monocalcium phosphate, with a progressive increase in the proportion of free phosphoric acid, pending equilibrium being attained, as is represented by the reversible reaction, thus:



¹ *Journal of American Chemical Society*, 28, 1220 (1906).

The liquid and solid phases vary according to the degree of saturation. Up to the saturation point there is a liquid phase consisting of water, monocalcium phosphate, and free phosphoric acid, with a solid phase consisting only of dicalcium phosphate, formed by hydrolysis of monocalcium phosphate. Beyond the saturation point, with increasing quantities of calcium oxide and phosphoric acid,

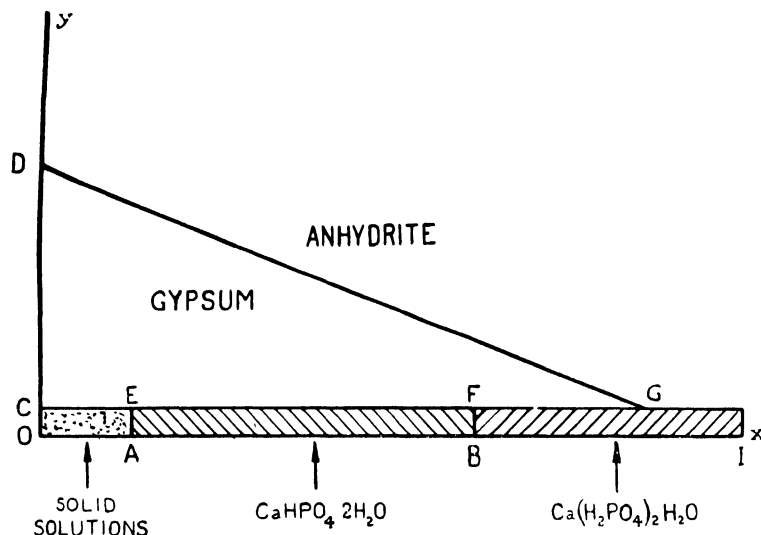


Fig. 7.—DIAGRAM RELATING TO THE FOUR-COMPONENT SYSTEM
(CaO, H₃PO₄, H₂SO₄ and H₂O)

acid, the liquid phase remains undisturbed, while the solid phase tends to increase in amount, with an increase of monocalcium phosphate. Temperature also plays a part. Following an increase of temperature, further decomposition of the monocalcium phosphate is effected, while the solubility of the dicalcium phosphate is augmented at the expense of the solid phase.

✓ *Chemical Changes as relating to Commercial Tricalcium Phosphate*

What does an examination of the chemical changes in the mixer and den reveal when ground rock phosphate is acted upon by sulphuric acid?

Many are the theories which have been propounded from time to time in explanation of the action in question.

Where an excess of sulphuric acid is used, there is reason to believe that the following reactions represent what takes place :

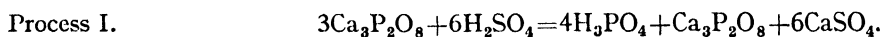
- (1) $\text{Ca}_3\text{P}_2\text{O}_8 + 3\text{H}_2\text{SO}_4 = 3\text{CaSO}_4 + 2\text{H}_3\text{PO}_4$.
- (2) $\text{Ca}_5(\text{PO}_4)_3\text{F} + 5\text{H}_2\text{SO}_4 = 5\text{CaSO}_4 + 3\text{H}_3\text{PO}_4 + \text{HF}$.
- (3) $\text{Ca}_5(\text{PO}_4)_3\text{OH} + 5\text{H}_2\text{SO}_4 = 5\text{CaSO}_4 + 3\text{H}_3\text{PO}_4 + \text{H}_2\text{O}$.

If a chloro-apatite or an organo-apatite is present, as contrasted with a fluoro-apatite, then equation (2) needs to be modified accordingly.

Where there is a deficiency of sulphuric acid, and the rock phosphate is incompletely dissolved, then evidence exists for the view that the reactions occurring are :

- (4) $\text{Ca}_3\text{P}_2\text{O}_8 + 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = 2\text{CaSO}_4 + \text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$.
- (5) $2\text{Ca}_5(\text{PO}_4)_3\text{F} + 7\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} = 7\text{CaSO}_4 + 3\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O} + 2\text{HF}$.
- (6) $2\text{Ca}_5(\text{PO}_4)_3\text{OH} + 7\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = 7\text{CaSO}_4 + 3\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$.

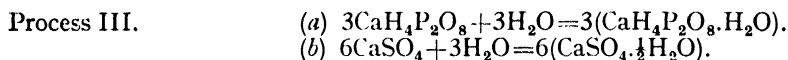
Following more recent study and experimentation, there appears to be good ground for the belief that the complicated reactions occurring between phosphate rock and sulphuric acid (disregarding the minor reactions, which relate to the action of sulphuric acid on alumina, calcium and magnesium carbonates, fluorine, iron, and silicates, etc.) can best be represented by presupposing the existence of three distinct and separate processes, thus :



The phosphoric acid released attacks a further quantity of phosphate, producing monocalcium phosphate :



Contrary to former belief, the conditions in the den are such that gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, cannot be formed (*vide* page 12). It has now been clearly established that the setting of calcium superphosphate in the den depends on loss of sulphuric acid, phosphoric acid and water, on the formation of solid salts and the crystallisation of $\text{CaH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$.



It must not be concluded that the three principal foregoing reactions take place consecutively, or that they represent precisely what occurs, or that the reactions proceed to completion. Any such assumption could not be conclusively supported.

That the first reaction proceeds to completion is tolerably certain, but of the remaining three, the two important ones are essentially "time reactions," and proceed more slowly. They are accompanied by the characteristic solidification and drying of the mass in the den.

Referring now to equation (x) (see p. 00), various possibilities which concern practice can be considered.

An Excess of Water and Little Free Phosphoric Acid.—What may conceivably occur in this case will be that the superphosphate may be damp. The calcium salts will, however, have crystallised, as represented by the equations (a) and (b) above, and drying, accompanying an increase of temperature, however applied, will readily furnish a good product.

Large Excess of Water and Free Phosphoric Acid.—In this case crystallisation may be retarded, or altogether prevented. An attempt to dry by the application of heat will give rise to the formation of a further quantity of free phosphoric acid. This increase should, however, gradually disappear as cooling proceeds, with a material improvement in the quality of the product.

A. Aita,¹ in a long paper, discusses the reactions from the last-named viewpoint, and reaches the conclusion that "the free acid in a good quality superphosphate should not exceed 5 to 10 per cent of the total soluble P_2O_5 , and that the uncombined water should not exceed 12 per cent."

The presence of dicalcium phosphate may be deemed to denote a good product. Crystallisation is defective, and the physical properties impaired, when the free acid and water exceed the limits already defined.

What Affects the Free Acid Content?—The factors exerting an important influence in this connection are: (1) the proportions of rock phosphate and sulphuric acid, and (2) the amount of water, which is a function of the specific strength of the acid used, and the temperature at which the reaction in the den takes place. Obviously, the higher the temperature the greater the evaporation of water. Clearly these factors are within the control of the fertiliser manufacturer. It should not be difficult to locate any irregularity or abnormality in manufacture if a logical application of the foregoing equations, and the conclusions to which they undoubtedly point, is made.

To avoid erroneous inferences, it will be well to enlarge further on this aspect.

To conclude, from an analysis of a sample of superphosphate immediately following manufacture that the major portion of the free acid was indicative of the use of an excess of sulphuric acid in connection with the mixing at the start, may prove unfounded. Excess sulphuric acid may conceivably be present in a freshly drawn sample, due to incompleteness of the reaction. Practical experience suggests that this is not a remote possibility in the case of a product which has been cooled too rapidly.

¹ *Ann. Chim. Appl.*, 10, 45 (1918).

The authors have known samples freshly drawn to show as high as 6 to 7 per cent of free acid as P_2O_5 , but after the lapse of a week this content was reduced to 4 per cent, and finally to 2.5 per cent. This reduction of free acid was accompanied by a corresponding increase of soluble phosphates.

The example cited above is peculiarly significant, as illustrating how, with Florida pebble and apatites, the attainment of equilibrium is somewhat sluggish. As a broad proposition, it can be said that equilibrium varies with the quality of the phosphate used. The harder the phosphate the less rapidly equilibrium is attained, and conversely, the softer the phosphate the quicker the attack by sulphuric acid, and the more rapidly equilibrium is reached. Stability of composition of the "super" in the heap can alone indicate the completion of the reactions. It is true that with the fine cutting of the finished product, which is now a feature of several of the mechanical dens and accessories, finality as regards the completion of the chemical reactions is tolerably rapid.

Determination of Free Acidity.—The work which Dr. Lehrecke of Kemiska Patent, A. B. Landskrona, has undertaken to ensure the more rapid determination of the free acidity of calcium superphosphate should be helpful to technicians. It is true that the free acidity of calcium superphosphate can be determined by one or two methods. The usual one is to extract the superphosphate with water and to determine the free acidity by titration, after suitable precautionary measures have been taken. Although this method gives significant and reproducible results, it suffers from the defect that it is not absolute. The shaking of the superphosphate with a large volume of water necessarily changes the conditions of equilibrium. It would appear, however, that the reaction is too slow to alter the free acid content appreciably during analysis (this objection applies also to the ether and cyclo-hexanol methods).

The other method consists of digesting the superphosphate in an inert solvent, which dissolves only phosphoric acid and allows of titration. Such solvents are ether and cyclo-hexanol. Ether involves a preliminary drying of the superphosphate—a procedure which alters the amount of free acid present. Cyclo-hexanol does not necessitate drying, and hence is more promising. Both methods give the total acidity. To attempt to discriminate between sulphuric acid and phosphoric acid in the total acidity is not an easy matter.

That sulphuric acid is present to a small extent in calcium superphosphate is not unlikely, since it is a complex equilibrium mixture derived from H_2SO_4 and $Ca_3P_2O_8$. But that it occurs to a much larger extent in calcium superphosphate containing a great deal of free acid is open to doubt. The usual method of deciding this is the use of some indicator, such as metanil yellow. This test, however, serves a useful purpose in that it indicates with certainty whether too much sulphuric acid has been used in the mixing, and it is suggested that advantage should be taken of this method more frequently than is the case, in order to economise the use of sulphuric acid in the manufacture of calcium superphosphate.

The minor reactions now call for attention. Taking these in order of importance, one comes to calcium carbonate.

Calcium Carbonate.—When sulphuric acid acts upon phosphates containing calcium or magnesium carbonates, the carbonates are first attacked with the formation at the outset of anhydrous calcium sulphate and the release of carbon dioxide. Two advantages accrue from this reaction, in so far as they affect the ultimate product—calcium superphosphate.

The heat evolved certainly aids the reaction and favours complete decomposition, and the passage of the gaseous CO_2 through the mass gives to it a porosity which assists drying, and conduces to a desirable mechanical condition. Subsequently, the anhydrous calcium sulphate may undergo hydration, with the formation of gypsum. This reaction being an exothermic one, it gives an added temperature to the mass undergoing decomposition.

The form in which the carbonates exist in various raw phosphates differs somewhat. In some phosphates it exists as calcium carbonate, although in a few cases—notably those of Carolina and Florida—it is found in the form of magnesium carbonate.

It has been affirmed by some fertiliser chemists that more than 5 per cent of carbonate acts adversely in the production of an abnormal amount of gypsum, which is prejudicial to the mechanical condition of the final product. Apart from this, acid is consumed to little effective purpose, besides which, one has to pay freight, handling, and other such expenses for a diluent which might conceivably be purchased and added at less cost.

With those phosphates which contain little carbonate, it will be found that the reaction with sulphuric acid is sluggish, practically no heat of reaction being evolved. In such cases it is preferable, nay, indeed, it can be said that it is established practice, to mix a low-grade phosphate, containing a higher content of carbonate of lime, with it.

The reactions involved when calcium carbonate and magnesium carbonate are decomposed by sulphuric acid are simple, and free from the complications seen in connection with calcium phosphate. They may be represented thus :



Calcium sulphate may crystallise with two molecules of water to form gypsum, and magnesium sulphate may crystallise with seven molecules of water to form a crystalline compound—Epsom salts.

It is known that magnesia occurs in small quantities as tribasic or neutral phosphate. The resulting magnesium acid phosphate is not deliquescent, like sodium bisulphate and other such compounds, neither is it decomposed by water.

Fluorine.—Fluorine, either as calcium fluoride or apatite, is found as a constituent of a large number of mineral phosphates. The chemical reaction which takes place on treatment with sulphuric acid is indicated on p. 37, as also are those which develop subsequently, following the action of hydrofluoric acid on silica, and the subsequent hydrolysis of the silicon tetrafluoride.

It is unnecessary, therefore, to elaborate this aspect further, except to say that silicates of lime and alumina are found in some rock phosphates, and such silicates are either attacked by sulphuric acid or by phosphoric acid, but only very sluggishly.

However, it is not inconceivable that some such slow reaction may explain part, at least, of the reversion of water-soluble phosphates in superphosphate—an aspect which will be dealt with at greater length in Chapter XI.

Chlorides and Iodides.—Apart from what is termed a “true apatite” ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), one finds in mineral phosphates other bodies of a somewhat similar composition, in which chlorine, iodine, and the hydroxyl group are substituted for fluorine.

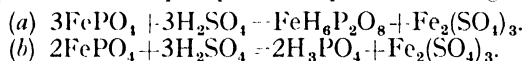
Normally, chlorides and iodides, on the application of sulphuric acid, will give rise to the production of hydrochloric acid and hydriodic acid. The last-named being subjected to partial oxidation by the oxygen of the air, will give rise to the evolution of iodine, which can readily be recognised by the characteristic violet tinge which it imparts to the gases evolved from the mixer and den.

Iron and Alumina.—In Chapter XI reasons will be found why careful attention should be paid to the contents of iron and alumina in mineral phosphates, which it is proposed to produce.

Not only are these bodies responsible for a relatively high consumption of sulphuric acid, but they also account to an important extent for the phenomenon of retrogradation.

The iron exists for the most part as ferric phosphate, although cases are known where it takes the form of pyrites, as is exemplified by Tennessee phosphates. Magnetite may also be present.

On treatment with sulphuric acid the phosphates in question undergo the following decomposition :



It has been suggested that where the oxide of iron content of a mineral phosphate does not exceed 2 per cent, little disability will accompany the use of such a raw material, inasmuch as to that extent calcium phosphate will remain in solution.

There is, however, the possibility of ferric sulphate acting upon monocalcium phosphate, with the consequent formation of ferric phosphate. This last-named compound exists in two forms—hydrated and dehydrated.

If there is a deficiency of water during the hydration of calcium sulphate to the crystal form—gypsum—water will be abstracted from the ferric phosphate, and this will render the latter considerably more difficult of attack by sulphuric acid. One attribute of alumina compounds is that they are sluggish in action, and hence their tendency to contribute to reversion—an aspect already referred to under this heading.

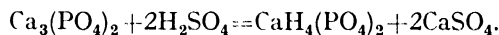
Organic Matter.—The theory is held that all phosphates are of organic origin, and in proof of this it is urged that when triturated to an impalpable powder, or when dissolved in acids, they all give a characteristic smell, somewhat resembling that of paraffin oil. From this it is assumed that these deposits are not of great antiquity, and that what metamorphosis has taken place can only be slight.

What concerns us at this juncture is whether any impaired fertilising value results from the attack of such organic matter by sulphuric acid. There appears to be a unanimity of opinion that, apart from the charring of organic matter by acid, little else ensues.

Despite the fact that much of the foregoing constituted part of our original treatise, the need for revision has not been insistent. Nevertheless, there has been published, by A. Sanfourche, an interesting contribution entitled, "Observations as to superphosphate: the gaps in our knowledge of this subject." This is given in detail below, as representing current information. The authors are indebted to the International Superphosphate Manufacturers' Association for these particulars, and acknowledgment is hereby made.

A survey of the chemical composition and physical condition of superphosphate, indicating the difficulties encountered in obtaining by analysis the information necessary to permit of its constitution being understood.

The reaction which gives birth to superphosphate, reduced to a rough outline, consists in the attack of tricalcium phosphate, an essential constituent of natural phosphorites, by a suitable proportion of sulphuric acid, having for result the production of monocalcium phosphates:



It might, therefore, be considered at a first glance that superphosphate is formed essentially of monocalcium phosphate and sulphate of calcium; many other substances, however, enter into its composition, arising mainly from the secondary constituents of the phosphorites, and to a smaller degree, from the impurities of the sulphuric acid. In a normal superphosphate, there are usually to be found:

Monocalcium phosphate, to the extent of 23 to 30 per cent according to the richness of the phosphorite used; accompanied by free phosphoric acid, it produces "water-soluble phosphoric acid," which in certain countries is the only condition to which a commercial value is attached, and which in others is at any rate considered as having a greater value than that of other forms of phosphoric acid. Monocalcium phosphate is for the greater part contained in the solid phase of superphosphate, although a considerable portion is found in saturated solution in the liquid phase.

Dicalcium phosphate is found in small, although not negligible quantities; it constitutes, with the monocalcium phosphate, free phosphoric acid and wholly or partly earthy phosphates, the portion known as "citrate-soluble phosphoric acid," or assimilable phosphoric acid.

Tricalcium phosphate, of which the always small proportion decreases as the superphosphate matures, is contained in the unattacked residue, either on account of some large grains of phosphate having escaped the action of the acid, or the proximity of other salts having protected them.

Free phosphoric acid is found in the form of a relatively concentrated solution in the liquid phase. It comes from the deliberate excess of sulphuric acid at the time of manufacture, but it has also another origin. Its quantitative analysis is amongst those which have led to the greatest number of investigations, and it will be seen that its extraction alone constitutes a delicate problem.

Sulphate of calcium constitutes about half of the weight of superphosphate; we shall show later that it is far from being the inert body which it is generally considered; its degree of hydration, the importance of which in connection with the physical condition of the superphosphate can be immediately grasped, has been considerably disputed. Superphosphates known as "double," "treble," "concentrated," which are manufactured by attacking natural phosphates with phosphoric acid, contain little if any calcium sulphate, and their physical properties are thereby completely transformed.

Iron and aluminium as well as *chromium*, of which very small though calculable quantities are found, for the portion attacked, as phosphates in the liquid phase, and otherwise as free or combined sesquioxides in slag; in spite of their relatively low proportion, iron and aluminium have a great influence on the physical condition of superphosphate, and even on the analytical results.

Magnesium, of which certain phosphorites (Gafsa) contain as much as 0.5 per cent, is found again in a corresponding proportion in superphosphate, generally in solution in the liquid phase.

Alkaline metals, particularly *sodium*, may be met with in superphosphate; their source is generally the sulphuric acid, when the manufacture of this involves direct use of sodium nitrate, although small quantities may also come from the phosphorites.

Fluorine, a normal constituent of the apatite contained in phosphorites, is partly eliminated as silicon fluoride during the attack by sulphuric acid; but a considerable proportion remains in the

superphosphate. No particular trouble has been taken to ascertain the condition of this fluorine, it having been supposed to remain in the slag in the form of free calcium fluoride, or as apatite which has escaped attack.

Small quantities of *chlorine* sometimes accompany the fluorine in the phosphorites.

Silica is mostly found in the form of quartz, but a fraction might be found in the phosphorite in the form of silicates ; at the time of the sulphuric acid attack, this fraction is more or less completely eliminated in the form of silicon fluoride, whereas the quartz is hardly touched.

Organic matter, evidence of the animal origin of the phosphorites, subsists in great measure in superphosphate, in the form of unknown combinations. A large number of quantitative analyses of carbon have proved to contain between 0.50 and 1 per cent of this element ; this may correspond to a double content of organic matter, the latter being probably in a state of advanced condensation.

Other bodies in very small quantities are frequently found in superphosphate, introduced either by the phosphorite, such as iodine and manganese, or by the impurities of the sulphuric acid, such as *nitric compounds, arsenic, selenium*, etc. ; from our point of view, it does not seem that they can affect the constitution of the superphosphate, because of their minute proportions, but an influence upon the vegetation has sometimes been attributed to them. This aspect of the subject has been treated in full in a recent paper by Hill, Marshall, and Jacob,¹ who have identified and estimated these elements in different American phosphorites and in the phosphoric acid extracted therefrom.

We shall not do more than mention the carbonates and free sulphuric acid, which should not be found in a well-manufactured superphosphate; the former would indicate a lack of acid, the latter an excess, or else an incomplete attack either through faulty contact or in consequence of insufficient fineness of the phosphate.

Superphosphate, at the time of its manufacture, has the appearance of a pulp, it is a more or less plastic mass while still fresh, that is to say for a variable period during which the reactions are taking place, and finally, when dry, is a coarse-grained powder. In reality, however dry it may appear, it always retains a liquid phase, the proportions of which vary considerably (from a few units to 20 per cent), and we shall see later that there may also be a colloidal phase, which certainly has a great influence upon its outward appearance and its physico-mechanical qualities. A small fraction of this liquid phase may be extracted by high pressure if the superphosphate is not too dry ; in this way a green liquid is obtained (1 cc. per kg. of superphosphate) of which the following are a few analyses :

	1	2	3	4
Density at 20°	1.440	1.440	1.477	1.463
Total P ₂ O ₅	33.0%	30.0%	32.1%	30.7%
Free P ₂ O ₅	18.0	9.5	15.5	11.8
Fe ₂ O ₃ , Al ₂ O ₃ , Cr ₂ O ₃	4.0	5.9	2.8	1.9
CaO	2.5	2.0	3.0	3.9
MgO	—	—	1.1	1.4
Alkalis (in Na ₂ O)	—	—	1.2	0.6

1. Superphosphate pressed on the day of its manufacture.
2. The same pressed at the end of 15 days.
3. Another superphosphate pressed 1 day after manufacture.
4. The same as 3, pressed at the end of 6 days.

It is fairly probable that the solution obtained by squeezing out does not exactly represent the liquid phase as it exists in the superphosphate, firstly, because of the selective adsorption of the constituents of the liquid phase by the solid elements with a highly developed surface where the capillary actions must be intense ; secondly, in consequence of the conversions which the mode of extraction may provoke ; as a matter of fact, Spring² has shown that the mono-basic phosphates of calcium,

¹ Hill, Marshall and Jacob, *Ind. Eng. Chem.*, 1932, Vol. xxiv, p. 1064.

² Spring, *Bull. Soc. Chim. Belge*, 1907, Vol. xxi, p. 91.

of sodium and lithium, when submitted to high pressure, liberate a certain quantity of phosphoric acid, leaving a more basic residue. In spite of these restrictions, the figures given above indicate that a concentration must be produced of certain elements in the liquid phase.

Finally, it might be thought that the constitution of superphosphate is well known, seeing that we are not ignorant of any of the bodies which it contains; nevertheless, we know but little about it, however astonishing that may seem when one remembers the great number of scientists and industrialists who, for more than a century, have interested themselves in this question. The reasons for this relative ignorance may perhaps be of two kinds: 1st, the elementary analysis is only of very slight assistance in comparison with that which would be obtained by immediate analyses concerning the different compounds in the actual state in which they exist; but little is known of methods suitable for this purpose. Those which are most generally adopted have only a conventional value; although quite useful for commercial transactions, they can only lead to error if an attempt is made to base conclusions of a scientific nature thereon: thus it would be fallacious to consider as dicalcium phosphate the portion which is insoluble in water and soluble in citrate, or to attempt to calculate the monocalcium phosphate in accordance with the difference between the water-soluble phosphoric acid and the free phosphoric acid. If, moreover, it is borne in mind that the majority of analytical treatments alter or convert the product treated, it may be said that the analytical methods at present adopted¹ are not calculated to demonstrate the real constitution of superphosphate.² 2nd. Certain of the compounds present in superphosphate cannot, from the point of view of their reactions, be considered as if they were isolated, they are not without action upon one another, which complicates not only the study of the constitution but also the analysis. Examples of this are found directly an attempt is made to go further into the question, and we shall later on mention several of these; the most typical is the action of calcium sulphate, which might be thought to be inert, on the hydrolytic decomposition of the monocalcium phosphate, a subject treated in a previous paper. The speed of this decomposition is entirely modified when calcium sulphate is present, as is the case when superphosphate is treated with water; an account of the investigations concerning this phenomenon is given in a later paper.

To sum up: in the attempt to extend our knowledge of superphosphate, we worked in the two following directions:

(1) We studied the causes of disturbance of the analytical methods and tried to remedy this where we thought possible; we in some cases attempted to establish more precise or more convenient methods or to take better advantage of the old ones.

(2) We manufactured pure superphosphate or partial constituents of superphosphate, which simplified the problem by eliminating secondary bodies, and allowed us to verify the methods of analysis. These secondary bodies were subsequently studied, first in isolation, then mixed with pure superphosphate.

¹ In France these methods are regulated by the Report to the Ministry of Agriculture of January, 1897.

² Cameron and Bell, U.S. Department of Agriculture Bureau of Soils, *Bull.* 41 and 42. Aita, *Ann. Chim. Applic.*, 1918, Vol. 10, p. 45.



CHAPTER IV

CRUSHING AND GRINDING PLANT

RAW phosphate requires to be ground before acidulation. The fineness to which it is ground depends, to some extent, on the phosphate being used (whether African or Pacific), but to a greater extent on the process of acidulation.

There are three processes in general use to-day for the manufacture of superphosphate ; they are :

The Batch Process,
The Continuous Process,
The Oberphos Process.

With the batch process, where "Milch," "Sturtevant," or similar type dens are used, the phosphate is usually ground to a fineness of 80 per cent through a screen having 10,000 holes per square inch. When using Nauru phosphate the grinding is not so fine and manufacturers find that a good dry superphosphate can be made with this phosphate ground to a fineness of all through a screen having 1,600 holes per square inch.

In America, however, they favour finer grinding, which suits the Florida and Tennessee rocks ; there, they generally work to a fineness of 90 to 95 per cent through a screen having 10,000 holes per square inch.

Where the continuous process is in operation, using the Broadfield or Moritz type den, the phosphate is usually ground to a fineness of 70 to 80 per cent through 100 mesh British Standard Sieve.

About ten years ago a new system of manufacturing superphosphate was developed in the United States of America, known as the Oberphos process, and was a distinct departure from all previous processes. It was operated in this country for a number of years by Messrs. Fisons, Ltd., of Ipswich, and one of their subsidiary companies. The operating and maintenance costs, however, proved prohibitive, and the process was ultimately abandoned. However, in a work of this nature a description of the process may be of historical value, and it is dealt with in a subsequent chapter.

In the Oberphos process the phosphate rock is usually ground to a fineness of 97 per cent through a 60 mesh British Standard Sieve.

In European works, where phosphates from all parts of the world are used, the raw material may vary considerably in size. This is less marked to-day than it used to be, as most mines have installed preliminary crushing plants. Nevertheless, most grinding plants include a preliminary crusher which, if not actually used to full capacity at all times as a crusher, acts as an automatic feeder to regulate the feed to suit the capacity of the fine grinder.

Moisture affects the rate of grinding, and its influence is felt more markedly with some phosphates than with others. For instance, Floridan and Moroccan phosphates should not contain more than 2 per cent of moisture, whereas Gafsa may contain as much as 5 per cent without creating any difficulty.

Since the establishment of the superphosphate industry many different grinding machines have been installed and some have been in use for a longer period than others. In the early days, and in fact until quite recent years, the cost of manufacturing was not explored too carefully, but this does not apply now. Indeed, before any grinding plant is installed to-day guarantees of a very rigid kind are imposed on the manufacturer, as the cost of grinding is an all-important one.

The result has been that obsolete types have been superseded by machines consuming less power and involving less maintenance.

In this country and throughout Europe the Ring-Roll type of mill holds the field almost exclusively. In America it is also popular, but has a powerful rival in the Raymond mill.

These two types of mills, without doubt, are responsible for the grinding of 75 per cent of the world's phosphate supplies.

A modern phosphate grinding installation comprises a number of machines which will now be described in their sequence of operation.

As previously mentioned, the preliminary crushing of the rock is not so important as it used to be, as the Pacific phosphates now shipped seldom contain lumps larger than 4-inch to 6-inch cubes, whereas most of the African phosphates will pass a $\frac{1}{4}$ -inch screen. Jaw crushers which were necessary at one time are now ruled out, and *rotary crushers* are almost exclusively used. They necessitate a minimum of power, and have the advantage that when little or no crushing is required they act as automatic feeders to the plants. They cannot be choked, and take their own feed. They can be fitted with a receiving hopper on top, into which a grab or Fordson shovel can tip half a ton at a time.

It is a slow-speed machine and little power is required to drive it: the power factor averages from 1 to $1\frac{1}{4}$ B.H.P. per ton of rock fed.

With this type of crusher the dust created in the process of crushing is held within the machine itself and is not allowed to escape into the surrounding atmosphere.

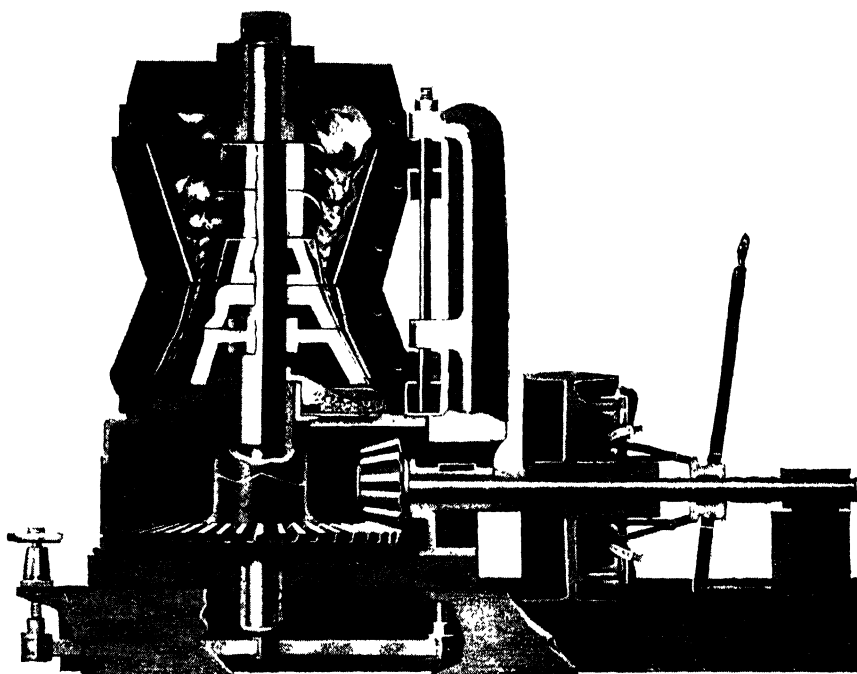


Fig. 8.—SECTIONAL VIEW OF ROTARY CRUSHER

Illustration Fig 8 shows the machine in general use. It is built on the open-door principle, which is clearly illustrated in the picture. This enables the machine to be opened out in a very short space of time, exposing wearing parts for inspection, and allows of the removal of any foreign matter which may have found its way into the machine by accident.

As will be seen from the illustration Fig. 8, the rock is crushed by gradual reduction. Firstly, as the teeth on the upper grinding nuts have a wide pitch a continuous nipping action is imparted to the material. In the lower cone of the machine a shredding or rubbing is imparted to the material, which tends to give a large percentage of "fines" in the product.

The central shaft can be moved up or down by means of the adjusting yoke under the crusher. This movement regulates the fineness of crushing.

As the rock is crushed and falls clear of the lowest grinding nut it is picked up by a scraping device and ejected from the discharge opening at the side of the machine.

When crushing phosphate rock the cones are usually set to give a product of approximately 1-inch cube and downwards, which is a suitable feed for the fine-grinding machine which follows.

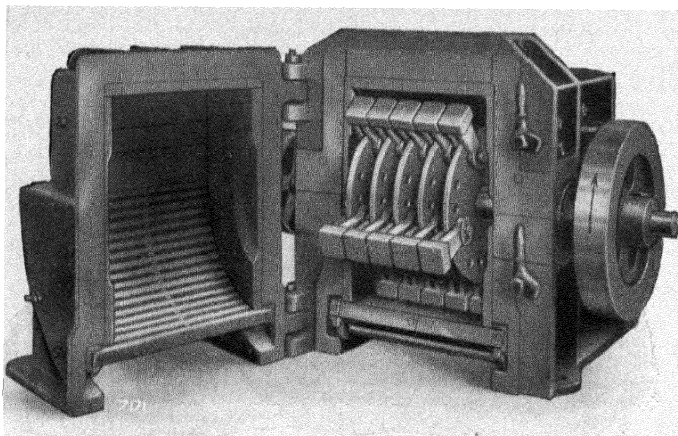


FIG. 9.—SWING SLEDGE MILL

Another type of machine, altogether different from the rotary crusher, is used in America for the preliminary crushing of hard rock phosphate. It is called a *swing sledge mill*, and is shown in Fig. 9.

It is built on the open-door principle, and is of massive design. It is fitted with coarse grate bars, which form the bottom of the machine and act as a rough sizing screen. The spaces between the bars are usually 1 inch wide. When used for this duty the mill is run at approximately 500 revolutions per minute, half its usual speed, and has a very large capacity. Further, it will take lumps of considerable size.

The hammers are made of special steel and are flexibly mounted, to give back in relief should a piece of iron enter the mill.

The shaft runs in Hyatt roller bearings.

The mill occupies very little headroom, which tends to minimise the depth of pit required to accommodate the elevator boot.

In the preliminary crushing of phosphate rock there is always a danger of tramp iron being present in the material and entering the crusher.

In rotary crushers, if this occurs, the friction clutch which drives the machine tends to slip, and as these crushers run at a slow speed they generally pull up before any serious damage occurs.

Magnetic Separators.—In modern plants the difficulty is entirely overcome by installing a magnetic separator.

One of those in common use is the Igranç magnetic pulley.

Fig. 10 shows the arrangement of one of these magnetic separators. The magnetic pulley is placed at the delivery end of the conveyor which carries the phosphate rock to the crusher. The belt is made sufficiently wide for the rock to spread over the width of the belt in a thin layer, approximately 2 inches thick. The magnetising of the pulley is accomplished by passing direct current through windings in the interior of the pulley. The current sets up a magnetic pull, which passes through the belt and attracts any iron or steel that may be contained in the rock. These pieces are held in contact with the belt until the latter leaves the pulley underneath. Here they are dropped, and may be collected in a box or other receptacle.

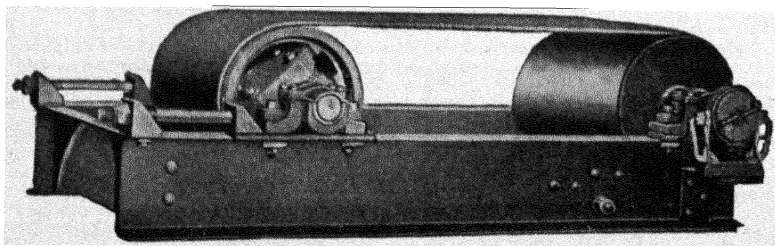


FIG. 10.—MAGNETIC SEPARATOR

Direct current is required to energise the magnetic pulley. Only a small amount of current is required, and this may be taken from any 110 or 220-volt direct-current electric circuit. It can also be made to work on a 500-volt direct-current circuit. When direct current is not available a small direct-current belt-driven generator can be installed at a nominal cost.

The pulley runs at approximately 38 revolutions per minute, and can be relied upon to remove all magnetic material varying in size from a nail up to 50 lb.

Fig. 11 shows a typical arrangement of a belt conveyor with a magnetic pulley at the delivery end. The hopper at the trailing end has adjustable sides, which regulate the amount of rock the conveyor belt picks up and delivers to the plant. The magnetic pulley ensures that no iron enters the crusher.

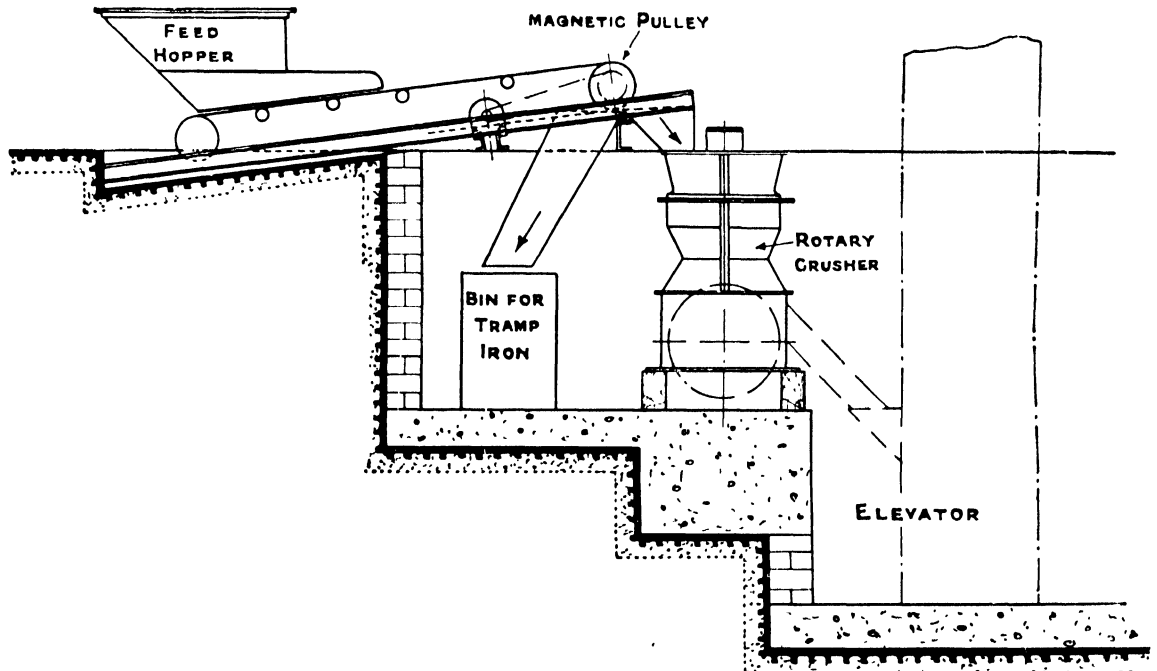


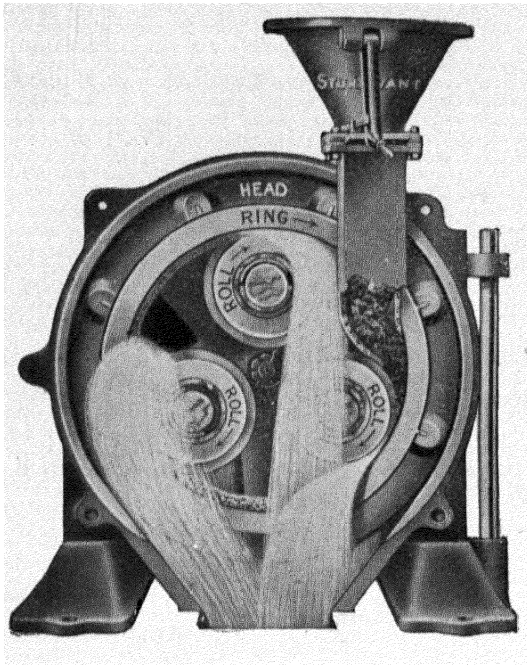
FIG. 11.—MAGNETIC SEPARATOR AND CRUSHER

Fine Grinding.—As previously stated, the Ring-Roll mill has superseded other types for the grinding of phosphate rock.

It operates on the principle of three grinding rollers, being kept in close contact with a grinding ring by means of spring pressure.

The ring revolves and the friction causes the rolls to rotate. The rock is fed between the first roll and the ring, and is circulated round by centrifugal force, a large proportion of it passing under the other two rollers. There is always a bed of material between the rolls and the ring, so that the metal surfaces do not come into contact and hence wear and tear is minimised. The pressure on the rolls is equal and opposite so that the ring is in equilibrium, which tends to reduce the power for driving. There are no internal screens to clog as separation is effected externally to the mill.

The illustration Fig. 12 gives a sectional view of a Ring-Roll mill and indicates the flow of the material. The first roll has a flat surface and will allow material up to $1\frac{3}{4}$ inch cube to enter the grinding



zone. The other two rolls have convex faces, as they produce most of the "fines."

The mill is so designed that the whole front opens like the massive door of a safe (see Fig. 13) and carries the rolls and all their parts entirely outside the mill. This is a great advantage when worn parts have to be changed.

The requisite grinding pressure is applied to the rolls by a central screw on the outside of the door, which adjusts the three rolls equally.

This type of mill is comparatively noiseless in action on account of its slow speed and steady pressure.

FIG. 12.—SECTIONAL VIEW OF RING-ROLL MILL

Fig. 14 is an outside elevation of the mill and shows the method of driving.

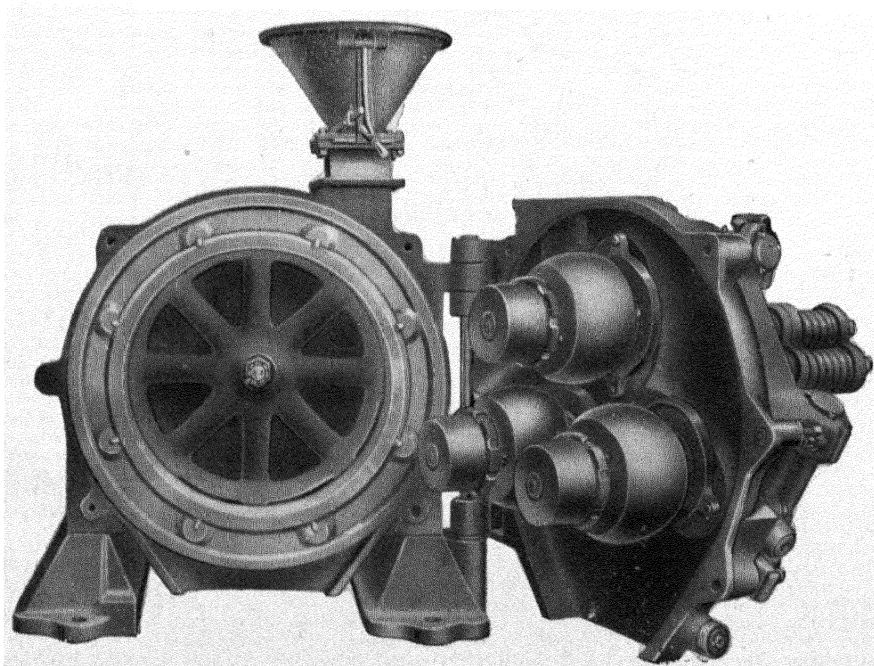


FIG. 13.—RING-ROLL MILL OPENED OUT

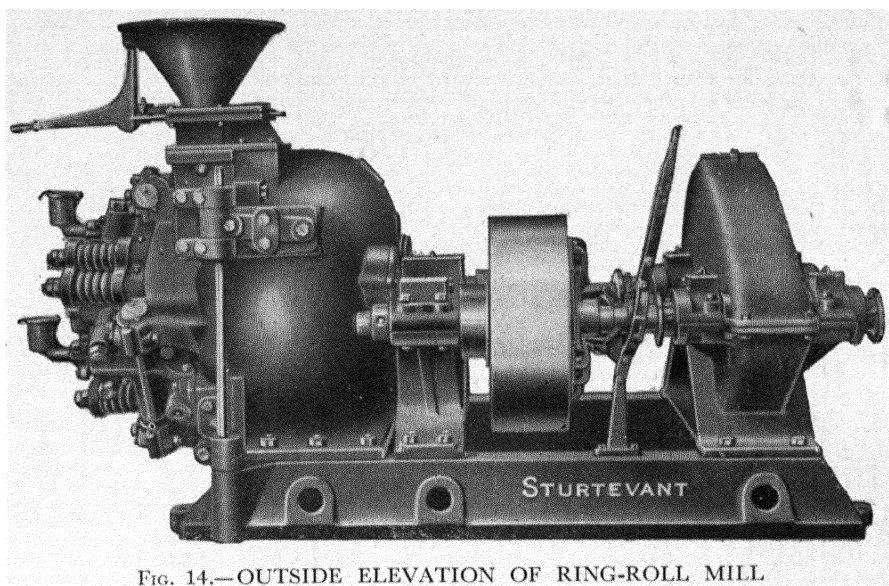


FIG. 14.—OUTSIDE ELEVATION OF RING-ROLL MILL

The following table gives the output on various phosphates and the horse-power required for driving the different units.

TABLE 12

Size of Mill.	Horse-power required for driving.	Output in tons per hour. Fineness, 80 per cent through 100 mesh B.S.S.				
		Florida Rock.	Pacific Islands.	Algerian and Moroccan.	Gafsa.	M'Dilla.
No. 1	25	2—2½	2½—3	3—4	4—5	3—4
No. 2	45	3½—4	4—5	5—7	7—9	5—7
No. 2 Duplex	90	7—8	8—10	10—14	11—18	10—14
Moisture not exceeding		2% .	2%	2%	5%	4%

The Ring-Roll mill does not give a finished product direct, and air separators, which have largely superseded screens, are used for extracting the fines, and the tailings are returned to the mill for further grinding.

Air Separation of Ground Phosphate Rock.—Fig. 15 gives a section of a modern air separator. These machines have been in use for nearly fifty years and were first used in the grain milling trade. Strange to say, there was little or no improvement on the early design until about twenty years ago, but since then there has been a remarkable development in their internal construction, and to-day the machines of well-known makers are extremely efficient.

In the separation of phosphate for acidulating purposes the efficiency averages about 80 per cent.

The machine operates in the following manner :

The crushed product from the grinding mill is fed through a chute in the top of the machine. A small deflector plate mounted on the vertical shaft serves to prevent the introduction of large lumps into the working parts. The material falls on to a distributing plate, directly under the inlet hopper,

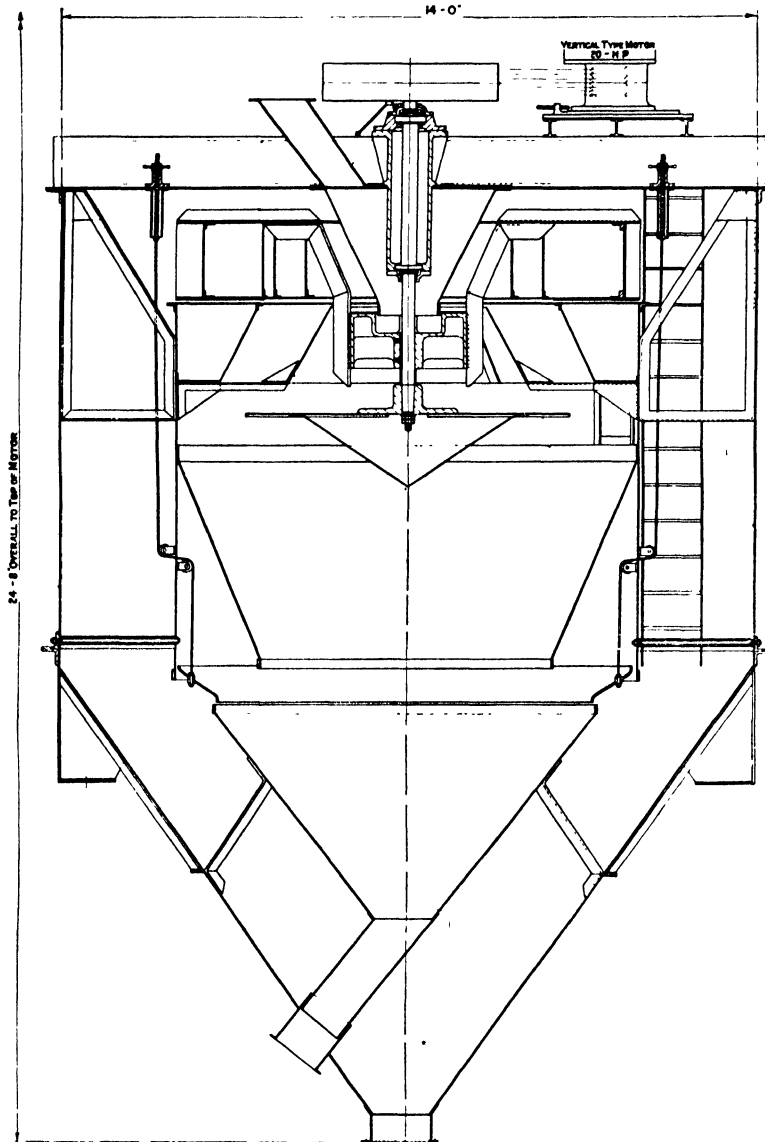


FIG. 15.—SECTION OF MODERN AIR SEPARATOR

and is then flung out by centrifugal force, forming a circular screen of falling material. The various deflecting rings and a serrated cone serve to loosen the fine from the coarse material. In the meantime, a horizontal fan, situated just under the top cover, creates a regular circulation of air through the falling screen of material. This air suction lifts the fines and whirls them round in the outer casing, where the ordinary action of a cyclone separator comes into force. The dust is flung against

the outer casing, gradually separates from the air, and finally falls through the outlet spout at the bottom. The oversize material, which has been too large for the air current to lift, falls down the inner cone or hopper, and is discharged through a separate outlet. An adjustable damper arrangement controls the opening, which allows the circulating air to return into the inner chamber.

These dampers are of various designs. The one shown in the machine in Fig. 15 is a flat ring, which is raised up and down by the screws and hand-wheels on top of the separator.

Fig. 16 shows another type of damper which consists of a series of adjustable tangentially-arranged vanes surrounding the inner cylinder in the path of the return air current. These vanes are said to accelerate the centrifugal effect, which helps the separation, and also tend to repel any dust particles which are likely to be entrained with the circulating air.

Fig. 17 is a complete view of one of these machines cut so as to show the inner working parts.

In all types of air separators, the product being separated is acted upon by three forces—the force of gravity, centrifugal force, and the force of the fan suction. The first two combine to prevent the third from lifting the material into the outer exhaust chamber. Thus any particles on which the combined action of gravity and centrifugal force is greater than the force exerted by the fan, will be projected outwards and downwards in the separating chamber, and discharged through the tailings spout.

The fineness of the product is varied in two ways—by regulating the speed of the vertical shaft, or controlling the damper. Alteration of the damper retards the speed of the circulating air, but has no effect on the centrifugal force.

Complete Ring-Roll Grinding Unit.—From what has been already written, it will be gathered that a Ring-Roll unit comprises a number of individual machines working in a closed circuit and to some extent is subject to modification to suit local conditions, such as height of buildings and position of storage silos.

A typical arrangement of a Sturtevant plant for the grinding of phosphate rock is shown in Fig. 18 and comprises the following machines :

Preliminary Rotary Crusher
Ring-Roll Mill
Air Separator
Circulating Elevator

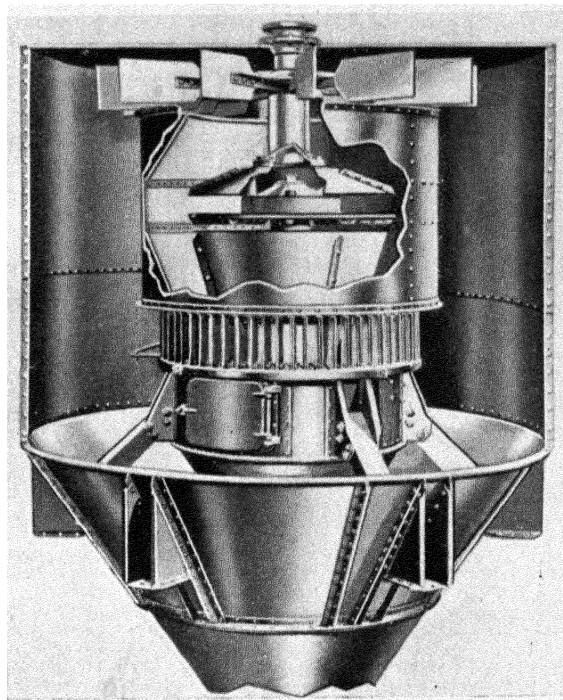


FIG. 16.—TANGENTIAL DAMPER IN AIR SEPARATOR

In addition to these items of plant, it is advisable to include a dust-collecting unit to ensure a clean atmosphere and safeguard the health of the workers. This dust unit comprises an automatic filter, suction fan, with the necessary hoods and piping connecting with the points where dust tends to arise.

Referring to Fig. 18, it will be observed that the mouth of the crusher is placed level with the ground. This enables the contents of a barrow or light truck to be tipped right into the mouth without the necessity of shovelling. This crusher is usually driven by a separate motor, so that when certain phosphates are being used, such as Moroccan or M'Dilla, the machine can be thrown out of gear ; the rock may then be fed direct to the elevator boot.

The product from the crusher is elevated to the air separator. In this machine the "fines" are extracted, and are usually conveyed to the storage silo by means of a worm conveyor, as shown in Fig. 18. The oversize material falls into the hopper over the Ring-Roll mill. The Ring-Roll mill is provided with a control valve for regulating the feed.

The product from the Ring-Roll mill falls into the circulating elevator, joining that from the rotary crusher, and is again elevated to the separator.

By this process the phosphate rock is continually circulating in an enclosed circuit, until it is ground finely enough to be taken out by the air separator.

The largest Ring Roll mill grinding plant in Great Britain is installed at the works of National Fertilizers, Ltd., Avonmouth, and consists of four No. 2 mills, with air separators and all the necessary accessories.

Dust Collecting. Reference has been made to the necessity of installing a dust-collecting plant. In addition to the value of the dust recovered, there are the advantages of increased efficiency and economies in upkeep of the grinding machinery.

The dust, if allowed to escape, gets into the bearings, interferes with smooth running, and accounts for unnecessary wear and tear.

Referring to Fig. 18, it will be observed that pipes are connected to the various machines where dust is likely to escape. These pipes are connected to an automatic dust filter and fan. This fan produces a draught sufficient to collect the impalpable dust (which ordinarily would be wasted) at the various points on the machines where dust is produced, and conveys it to a suction filter. The fan withdraws the dust-laden air through the filter, where the dust is arrested and collected, and the clean air is exhausted to the atmosphere. The suction fan is made of steel plate, as shown in Fig. 19, and the volumetric capacity is designed to suit the grinding capacity of the plant.

Fig. 20 shows an automatic filter in general use at superphosphate works. In this apparatus the cabinets are square in form, and each contains nine sleeves. These are held taut in the working position, and the shaking mechanism is so arranged that when the sleeves are allowed to fall slack a compression spring brings them back again to the normal position with a sudden jerk, which is effective in dislodging the dust. The operating mechanism is of simple design, and use is also made of atmospheric air in giving a reverse current through the sleeves during the time they are being shaken.

This type of filter requires about 1 h.p. to operate it, and it is possible to collect from a two-cabinet machine, which is the smallest unit, 5 to 6 cwt. of dust per day of eight hours. Without a dust-collecting plant approximately this quantity of impalpable powder would escape and constitute a nuisance.

The dust collected in the filter hopper is generally conveyed to the "fines" storage silo by means of a worm conveyor.

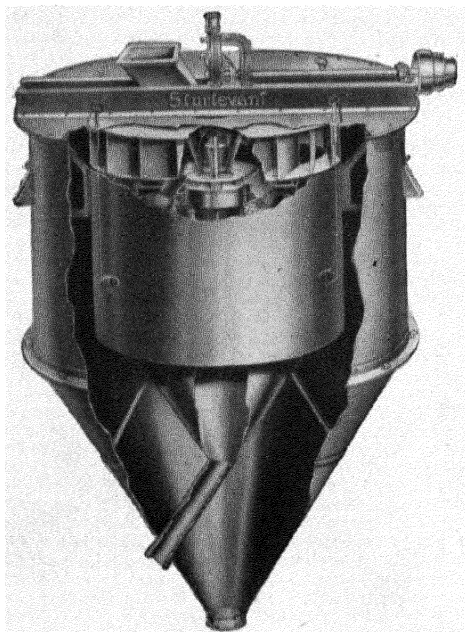


FIG. 17.—AIR SEPARATOR CUT TO SHOW INNER WORKING PARTS

The Raymond system of grinding.—In Raymond plants the pulverising and separating of the fine material by air are combined in one complete unit. The machines comprising this system are so interdependent and unchangeable that it is hardly possible to describe the grinding mill without continual reference to the separating equipment.

The grinding mill and separating plant are really one complete machine and indeed must be regarded as such for the purpose of description.

Fig. 21 shows a Raymond mill and cyclone collector.

As will be seen from the illustration, mechanical elevators are entirely eliminated.

The Raymond roller mills crush and pulverise the phosphate rock by gravity and centrifugal force. The manner in which this is accomplished will be understood by referring to Fig. 22.

The phosphate rock, which has been previously crushed to approximately $1\frac{1}{2}$ -inch cubes, is fed to the mill from a storage bin through the spout S into the automatic-feeding mechanism F. This

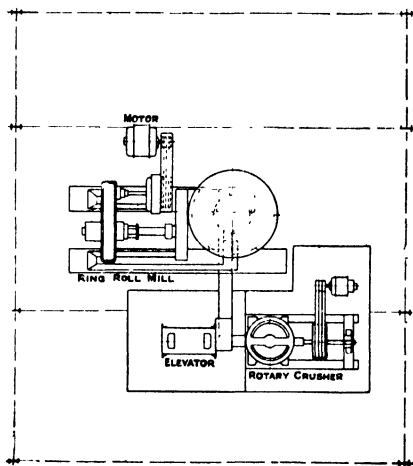
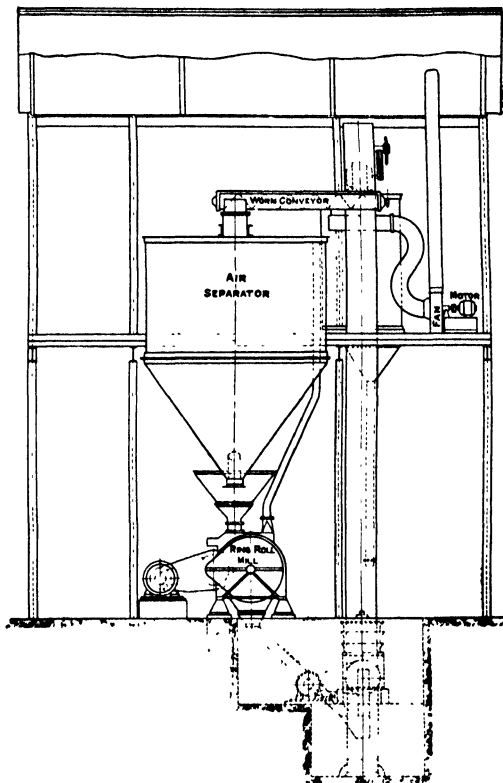
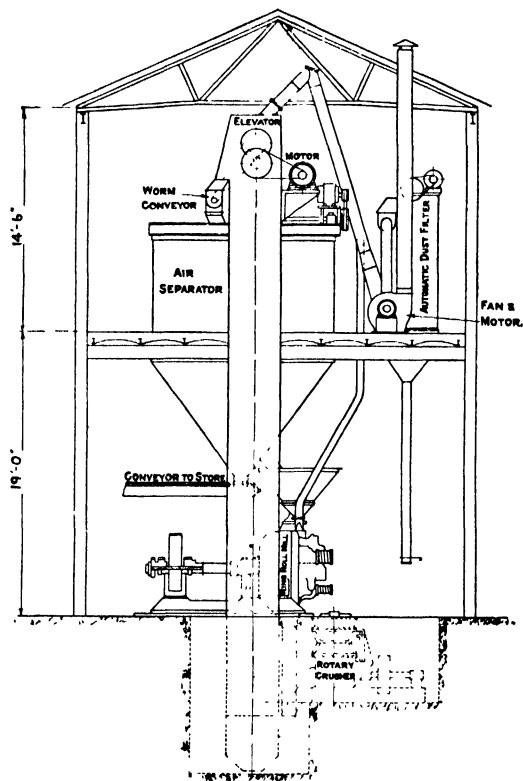


FIG. 18.—NO. 1. STURTEVANT GRINDING PLANT FOR PHOSPHATE ROCK

delivers it in the proper quantities to the grinding chamber G. Here it is caught by the manganese steel ploughs P and thrown up between the rollers R and the grinding ring B. One of these ploughs is located just ahead of each roller, so that a constant stream of material is forced between the rolls and ring.

The separation of the finely ground material from the coarser particles is accomplished by the constant stream of air drawn through the mill by the exhaust fan. The stream of air enters the mill through a series of tangential openings around the base of the grinding chamber, and passes upward

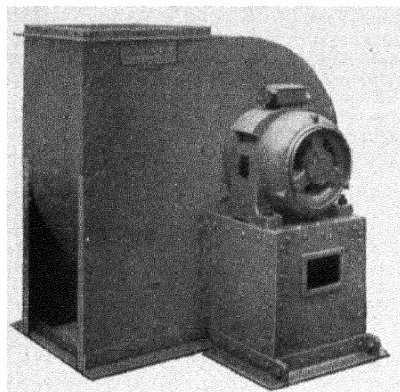


FIG. 19.—SUCTION FAN

FIG. 21.—RAYMOND MILL AND CYCLONE COLLECTOR

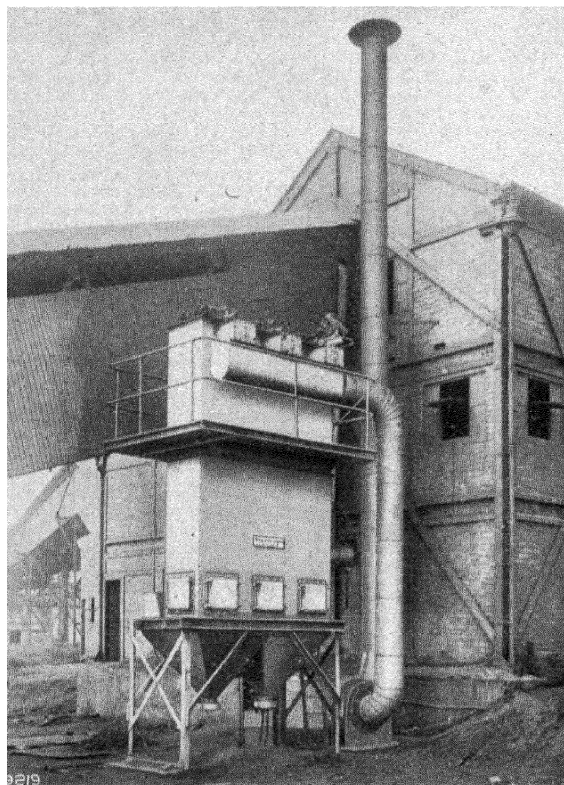
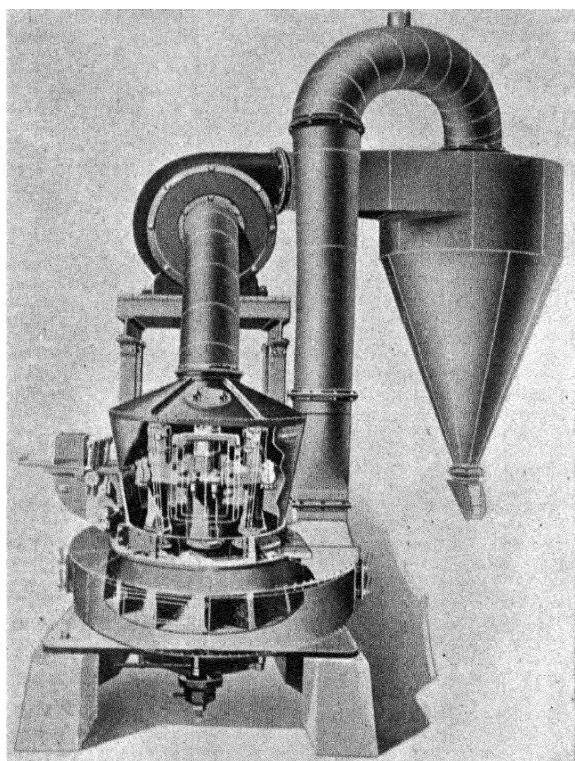


FIG. 20.—AUTOMATIC SUCTION FILTER

around the rollers R and the grinding ring B. In passing up it carries with it the finely pulverised material from the grinding chamber into the separator. The coarser and heavier particles fall back and are thrown up by the ploughs P, to be reground until reduced to the desired fineness. No fine material remains in the grinding chamber to clog the mill and prevent continuous operation on coarse material.

The operation is entirely automatic: the operator has only to see that the phosphate rock is fed to the mill at the proper rate. It is necessary to keep a considerable amount of material in the spout S to reduce the amount of surplus air entering the mill.

Like the other mills of the ring-and-roll type already described, there is always a constant stream of material between the rolls and the grinding ring, which prevents direct contact between the pulverising surfaces.

The finely ground phosphate rock is withdrawn from the mill by means of the exhaust

fan and blown into the cyclone, where it is deposited. The air returns from the top of the cyclone through the mill.

Where space is limited, the installation may be arranged with the cyclone adjacent to the mill, or it may be adapted to meet the conditions of any particular plant.

The coarse material (*a*) is used for acidulation, and the fine material (*b*) for direct application to the soil. Cost data are based on power at 3 cents per kw. hr. and labour at 50 cents per hour.

Phosphates.—Phosphate rock is generally pulverised for one of two major purposes, for direct application to the soil, or for acidulation with sulphuric acid in the manufacture of superphosphate. Table 13 gives the data for pulverising phosphate materials in a Raymond five-roller mill equipped with integral air separation, as previously described on pages 52, 53 and 54.

Throughout the preceding chapters, fineness in the term of mesh has been mentioned a great many times, yet it may be a confusing term, unless the screen standard is known.

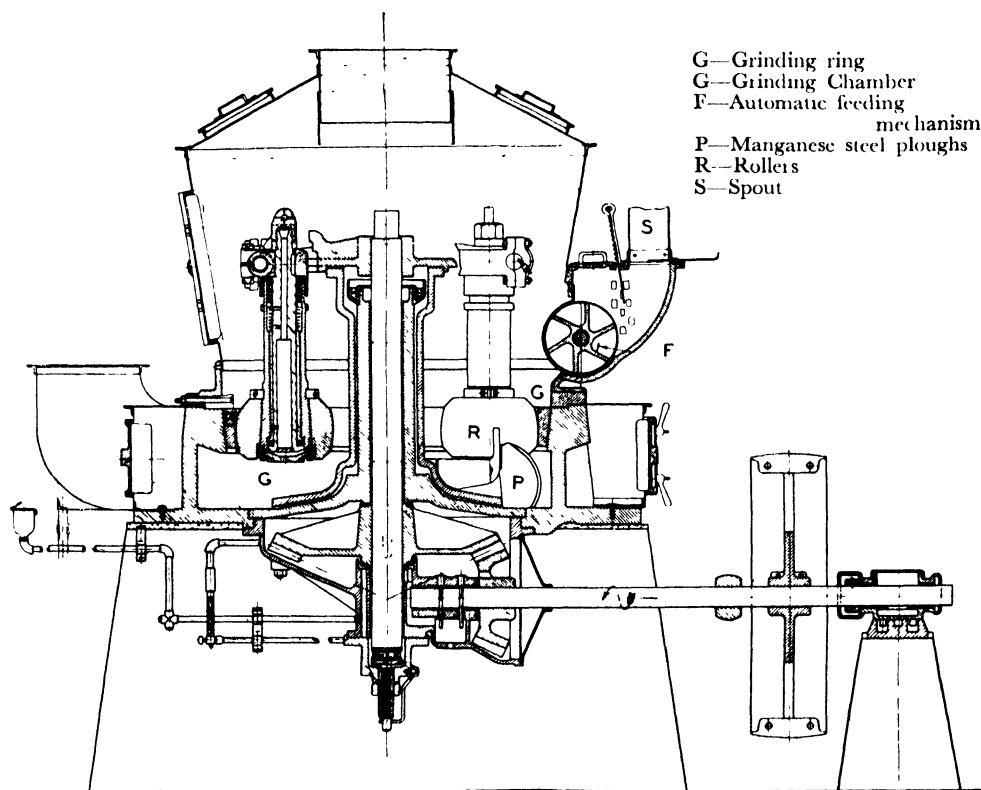


FIG. 22.—SECTION OF RAYMOND MILL

There are now three standard scales in common use. In Great Britain there are two standards in use, known as the I.M.M. sieves and the British Standard sieves.

In the United States of America the Tyler Standard Screen Scale is generally recognised, and has been adopted as the U.S. Bureau of Standard Screen Scales.

In the United States it is the practice to use a light or medium grade of wire for testing sieves, whereas in Great Britain, the I.M.M. sieves are made from the heaviest wire it is possible to weave.

These test screens are nearer to the actual cloth used in screening operations than the Tyler test screens, but the great objection is that in the I.M.M. series there is no relation or fixed ratio between the various sieve openings in the series. The ratio is not a regular one.

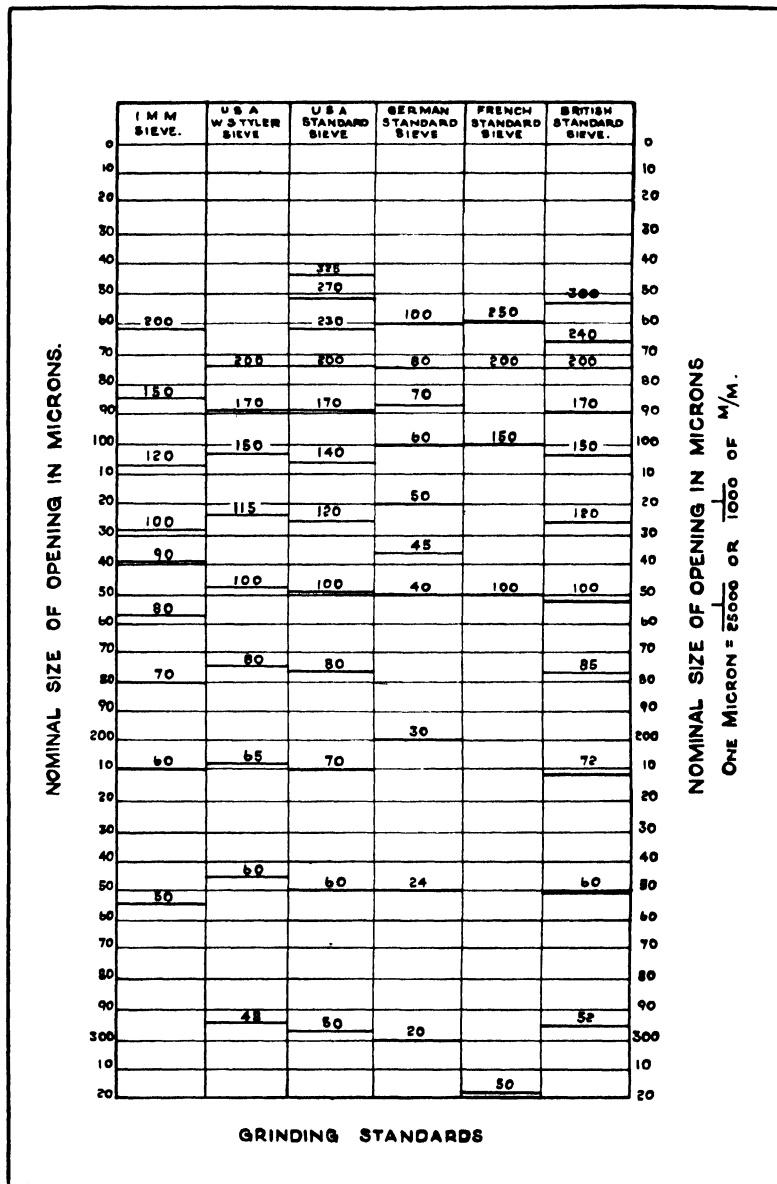


FIG. 23.—DIAGRAM OF STANDARD SIEVES

Table 15a on next page gives details of the I.M.M. screens.

Fig. 23 will show at a glance the comparative sizes of these different Standard screens.

TABLE 13

Five-Roller Raymond Mill. Capacities, Grinding Phosphate Materials

	Production, tons per hour.					
	(a) 90-95% through 60 mesh; 50-55% through 200 mesh. ¹	(b) 90-95% 200 mesh.	H.P.		Cost for power and labour, dollars per ton.	
			a.	b.	a.	b.
Algiers	7.5	—	13	—	—	—
Arkansas block rock	6.5	4	15	19	0.49	0.70
Belgium	8.5	—	12	—	—	—
Bohemia (apatite)	6.5	—	17	—	—	—
Canada (apatite)	6	3	18	26	0.61	0.85
Egypt	6.5	—	17	—	—	—
Florida (pebble)	6.5	3.5	17	24	0.51	0.73
Florida (hard rock)	7	4	17	24	0.48	0.68
Florida (soft rock)	—	5.5	—	15	0.42	0.59
Idaho	7	4	14	19	0.46	0.68
Kentucky	7.5	5	12	17	0.42	0.60
Morocco	8	—	12	—	—	—
<i>Pacific and Indian Oceans :</i>						
Angaur Island	8.5	—	12	—	—	—
Christmas Island	8	—	12	—	—	—
Marshall Islands	8.5	—	12	—	—	—
Makatea Island	7	—	12	—	—	—
Nauru Island	7	—	13	—	—	—
Ocean Island	7.5	—	13	—	—	—
Russia (Podolian)	6.5	—	13	—	—	—
Tennessee (blue rock)	7	4.5	14	18	0.46	0.65
Tennessee (brown rock)	7.5	5	12	17	0.42	0.60
Tennessee (grey rock)	8	5	12	17	0.42	0.60
Tennessee (phosphatic limestone)	7	4.5	14	18	0.46	0.65
S. Carolina	6.5	3.5	17	24	0.52	0.73
Tunis	8	—	12	—	—	—

The British Standard Sieve recently adopted by the British Fertiliser Manufacturers is a compromise between these two.

The Tyler Standard screens increase and decrease throughout the series in a fixed ratio. The openings increase in the ratio of M2 or 1.414. This ratio was recommended by Rittinger in his work on ore dressing. Table 14 on the following page gives the complete series.

In 1907 the Committee of Standards of the Institute of Mining and Metallurgy in Great Britain adopted a sieve series for testing purposes. The main purpose of this series seemed to be the manufacture of screens in such a way that the wires could not get out of place, having about 25 per cent of the screen as opening and the rest dead surface. It was assumed that if the size of wire were made the same as the screen opening, the wires would remain in position.

TABLE 14
The Tyler Standard Screen Scale
 Ratio M2=1.414

Size of opening.		Mesh.	Diameter of wire. Inches.
Inches.	Mm.		
1.050	26.67	—	0.149
0.742	18.85	—	0.135
0.525	13.33	—	0.105
0.371	9.423	—	0.092
0.263	6.680	3	0.070
0.185	4.699	4	0.065
0.131	3.327	6	0.036
0.093	2.362	8	0.032
0.065	1.651	10	0.035
0.046	1.168	14	0.025
0.0328	0.833	20	0.0172
0.0232	0.589	28	0.0125
0.0164	0.417	35	0.0122
0.0116	0.295	48	0.0092
0.0082	0.208	65	0.0072
0.0058	0.147	100	0.0042
0.0041	0.104	150	0.0026
0.0029	0.074	200	0.0021

TABLE 15A
I.M.M. Standard Laboratory Screens

Mesh, or apertures per linear inch.	Diameter of wire.		Aperture		Screening area. Per cent.
	Inches.	Mm.	Inches.	Mm.	
5	0.1	2.540	0.1	2.540	25.00
8	0.063	1.600	0.062	1.574	24.60
10	0.05	1.270	0.05	1.270	25.00
12	0.0417	1.059	0.0416	1.056	24.92
16	0.0313	0.795	0.0312	0.792	24.92
20	0.025	0.635	0.025	0.635	25.00
30	0.0167	0.424	0.0166	0.421	24.80
40	0.0125	0.317	0.0125	0.317	25.00
50	0.01	0.254	0.01	0.254	25.00
60	0.0083	0.211	0.0083	0.211	24.80
70	0.0071	0.180	0.0071	0.180	24.70
80	0.0063	0.160	0.0062	0.157	24.60
90	0.0055	0.139	0.0055	0.139	24.50
100	0.005	0.127	0.005	0.127	25.00
120	0.0041	0.104	0.0042	0.107	25.40
150	0.0033	0.084	0.0033	0.084	24.50
200	0.0025	0.063	0.0025	0.063	25.00

The following Table gives details of the British Standard screens which are the latest to be adopted:

TABLE 15B
British Standard Screens

Mesh No.	Aperture.			Diameter of wire.		S.W.G.	Approx. Screening Area per cent.
	Inch.	Mm.	Inch.	Inch.	Mm.		
300	·0021	·053	1/480	·0012	·030	49	41
240	·0026	·066	1/400	·0016	·041	48	38
200	·0030	·076	1/333	·002	·051	47	36
170	·0035	·089	1/288	·0024	·061	46	35
150	·0041	·104	1/240	·0026	·066	45½	37
120	·0049	·124	1/200	·0034	·086	43½	35
100	·0060	·152	1/168	·004	·102	42	36
85	·0070	·178	1/144	·0048	·122	40	35
72	·0083	·211	1/120	·0056	·142	38½	36
60	·0099	·251	1/100	·0068	·173	37	35
52	·0116	·295	1/84	·0076	·193	36	37
44	·0139	·353	1/72	·0088	·224	34½	38
36	·0166	·422	1/60	·0112	·284	31½	36
30	·0197	·500	1/50	·0136	·345	29	35
25	·0236	·599	1/42	·0164	·417	27	35
22	·0275	·699	1/36	·018	·457	26	36
18	·0336	·853	1/30	·022	·559	24	36
16	·0395	1·003	1/25	·023	·584	23½	40
14	·0474	1·204	1/21	·024	·610	23	44
12	·0553	1·405	1/18	·028	·711	22	44
10	·0660	1·676	1/15	·034	·864	20½	44
8	·0810	2·057	1/12	·044	1·118	18½	42
7	·0949	2·411	1/10	·048	1·219	18	44
6	·1107	2·812	1/9	·056	1·422	17	44
5	·1320	3·353	1/8	·068	1·727	15½	44

CHAPTER V

MANUFACTURE OF CALCIUM SUPERPHOSPHATE—MIXING PLANT

IN the early days of the superphosphate industry, the mixing of ground phosphate rock with sulphuric acid was carried out in a very primitive way.

The den consisted of a rectangular pit, usually made of brickwork. A measured quantity of sulphuric acid was run into the den. Meanwhile, the phosphate rock had been weighed and brought to the side of the den. While this was being shovelled in, men agitated the mass with rakes until it stiffened. Modern methods, which are subsequently described, are entirely different, due to the progress which has been made in chemical engineering.

It is necessary to describe firstly *the mixing equipment for the batch type of den*, as many of these are still in use, and later describe the process which is used with continuous type dens.

In the batch system the phosphate rock and acid are usually weighed, although in many factories the acid is measured in a graduated tank.

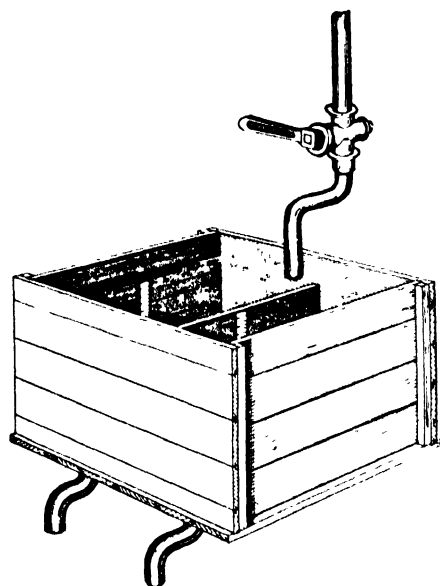


FIG. 24.—ACID MEASURING TANK

Two methods are employed for measuring the acid, but they have this fault in common—accuracy depends upon the operator and not upon the machine.

In some works a tank built of wood and lined with lead is used. There is a partition in the middle which does not extend to the top, thus making two tanks side by side, which hold about 6 cwt. of acid each. The acid pipe comes down to a point just over the partition at one end of the tank, and a swivel-cock is fitted on the end of the acid pipe which allows the acid to flow into either division of the tank. On one side of each division there are graduated marks to register the quantity of acid. Should the operator omit to notice that the correct amount of acid has flowed into the tank, it will only rise to a certain level above the mark, when it flows over the partition into the other tank. This might be termed a safety device. Each section is used alternately. There is a plug-valve in the bottom of each section to regulate the outflow, and these are operated by levers on the top.

Fig. 24 shows an acid-measuring device of this description.

In the United States of America they mix large quantities of sulphuric acid and phosphate rock at one time. Their mixers usually take approximately one ton of each.

Their acid-measuring tanks are therefore larger than those generally used in England, and they measure in a different way.

From the bottom of the tank a lead pipe is carried out to a convenient distance, and then a gauge-glass fitting is connected to this pipe. As the acid rises in the tank it also rises in the gauge glass, and as the latter is marked to indicate the quantity in the tank, the operator watches the glass to determine when to shut off the acid valve.

This system does not ensure complete accuracy, because a slight error in vision is multiplied many times in the acid tank.

Acid Weighers.—A semi-automatic acid-weighing scale made by the Sturtevant companies of England and America is the latest device of this kind, and eliminates any chance of error on the part of the operator.

A diagrammatic view of the machine is given in Fig. 25.

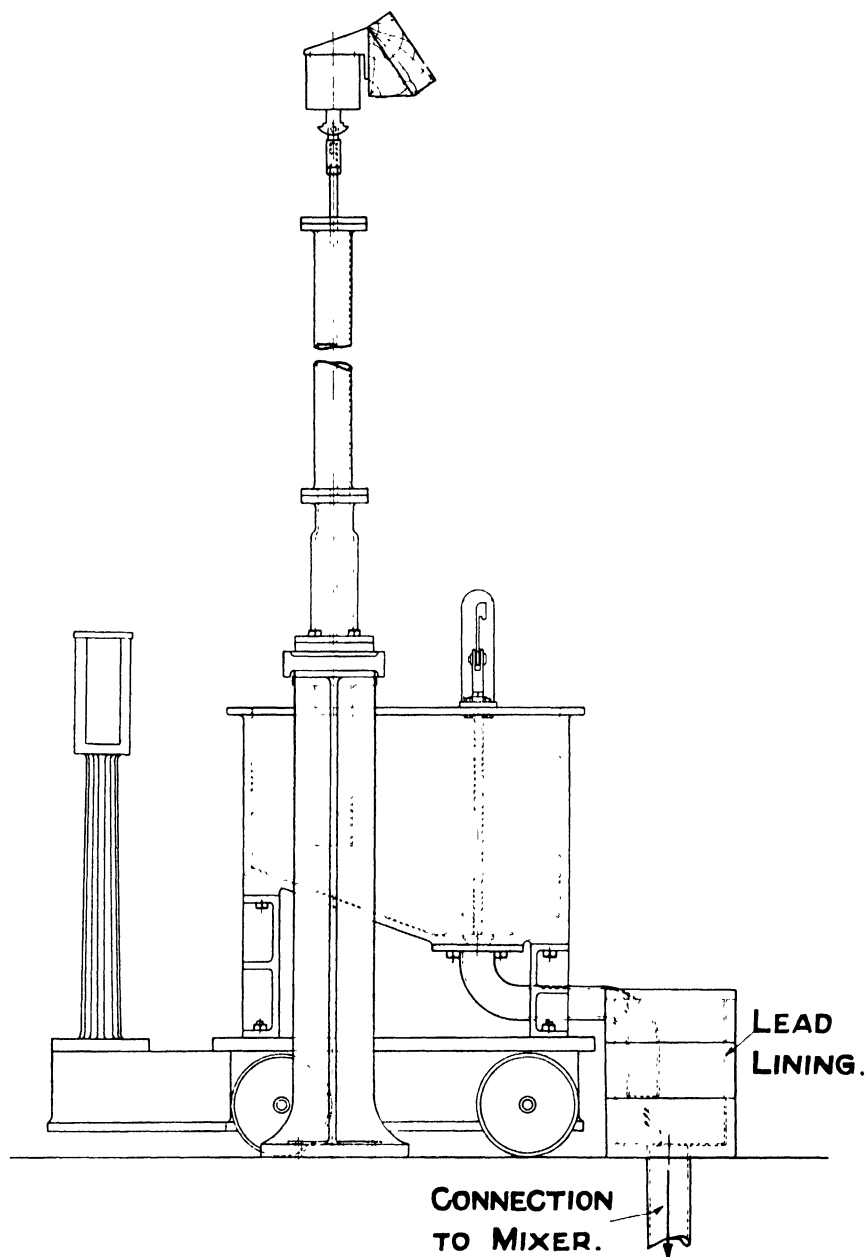


FIG 25.—STURTEVANT SEMI-AUTOMATIC ACID WEIGHER. DIAGRAMMATIC VIEW

It consists of an ordinary platform-weighing scale with the acid tank fixed on the weighing platform. The main acid supply pipe is shown entering at right-angles, with a cut-off valve within reach of the floor. The vertical stand pipe is of sufficient height to reach above the level of the acid

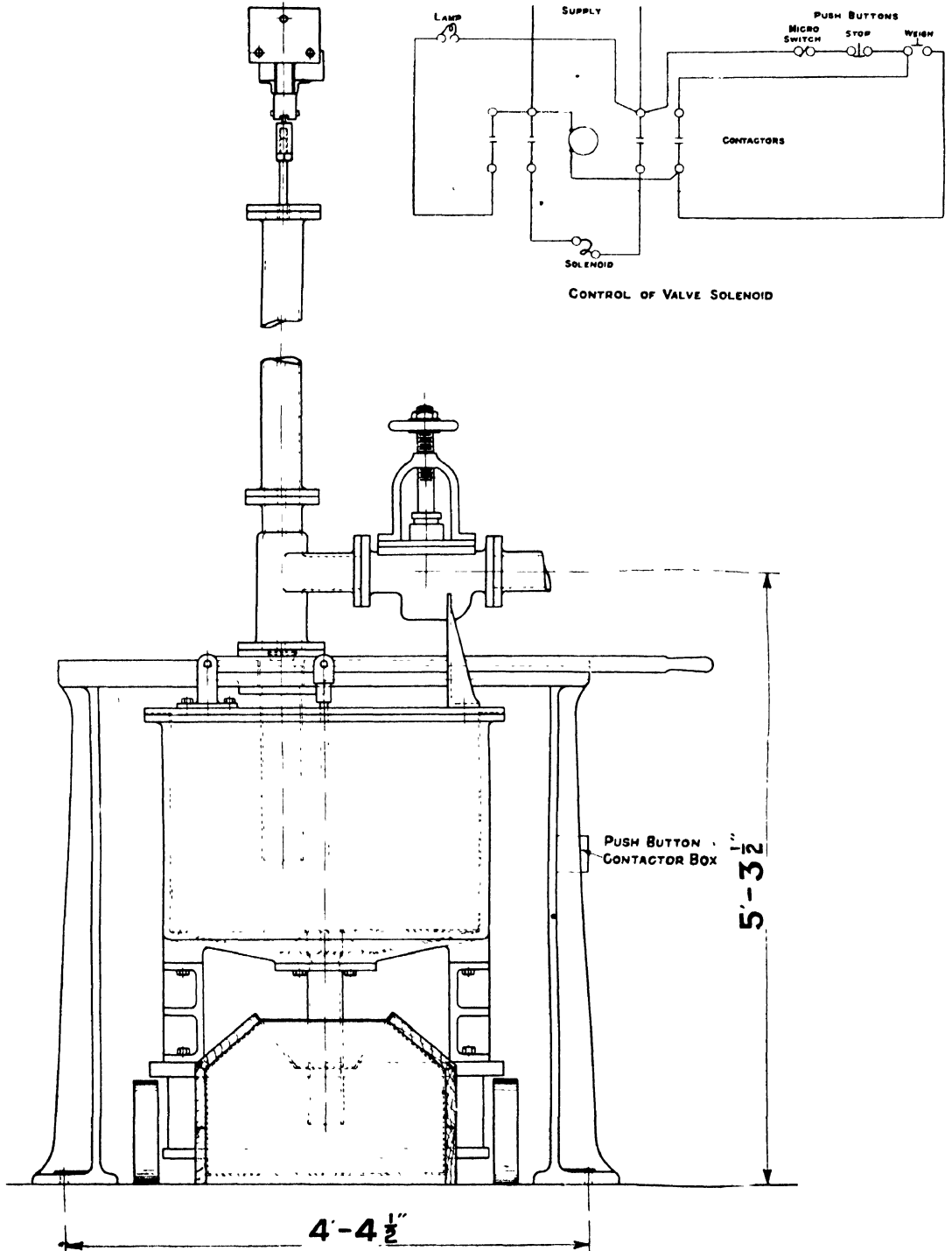


FIG. 26.—STURTEVANT SEMI-AUTOMATIC ACID WEIGHER

in the storage tank, and prevents overflowing when the main valve is open. The valve which controls the flow of acid into the weighing tank is situated below the junction of the main supply pipe and the vertical pipe. This valve is operated by the horizontal lever, which engages with the tappet rod secured to the valve. Just above the horizontal lever at one end is fixed a strong electro-magnet.

The electric circuit which excites the magnet is controlled by the movement of the scale beam. Underneath the weight carrier, two insulated rods are fixed which have their points dipping into two mercury pots. When the acid tank is empty the scale beam is in its lowest position, and the rods are dipping in the mercury and the electric circuit is "made," which excites the magnet.

At the commencement of the mixing operations let us assume the acid bowl is empty. The rods will then be in the mercury, and as soon as the main switch is closed, the electric circuit being complete, the magnet will become "excited." The horizontal lever is lifted up to the magnet which holds it, and in this position the valve is open and the acid flows into the tank. As soon as the quantity of acid flows into the tank to make the weight for which the scale is set, the scale beam begins to rise, bringing the rods out of the mercury. Immediately they are out the circuit is broken, the magnet releases the lever which is holding up the valve, and the latter drops on its seat, cutting off the supply

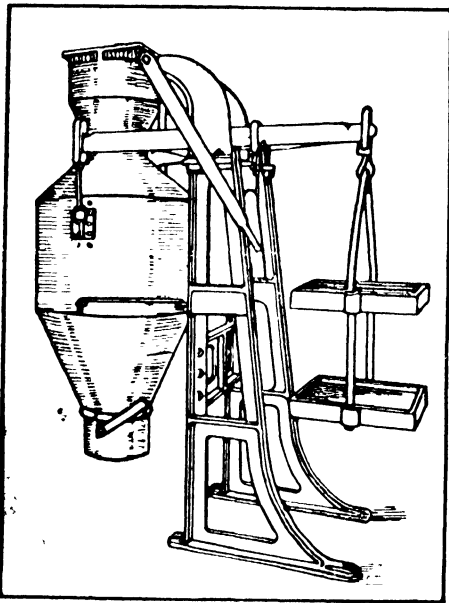


FIG. 27.—BAKEMA SEMI-AUTOMATIC WEIGHER

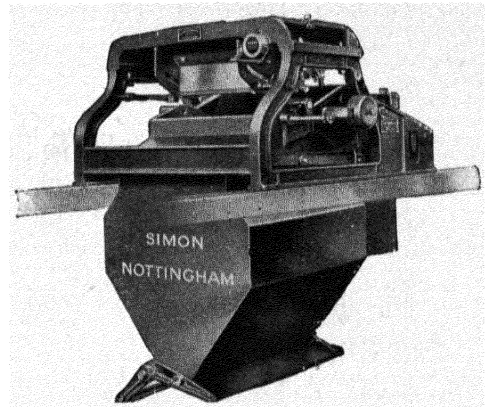


FIG. 28.—SIMON PHOSPHATE WEIGHING SCALE

of acid. A coloured lamp is fixed in the circuit, which enables the operator to tell at a glance when the next charge of acid is ready for the mixer.

The plug-valve in the bottom of the weighing tank is operated by hand, by means of the lever shown on top of the tank.

When the charge has passed into the mixer, the operator closes the plug-valve, lifts the horizontal lever up to the magnet, and the operation commences over again.

Fig. 26 shows another view of the apparatus.

Phosphate Weighers.—Weighing machines of various types are used for weighing the ground phosphate rock.

The Bakema semi-automatic weigher is illustrated in Fig 27.

It is a simple balanced scale. Weights corresponding to the charge of phosphate are placed on the two carriers on the right. The container is cylindrical in form, with valves at the top and bottom. As soon as the charge of phosphate has passed into the container, and the latter begins to deflect, an automatic device shuts off the supply valve at the point of balance. The discharge valve is operated

by hand, and when the container is empty the inlet valve is again opened by the hand lever shown. The container is built in the form shown, to facilitate the flow of ground rock, which has a tendency to adhere to angular corners if it is slightly damp.

The Simon phosphate weighing scale is illustrated in Fig. 28, and is automatic in operation. It is designed for weighing 2 cwt. batches.

This machine is usually installed as shown in Fig. 29. Immediately above the scale there is a small storage hopper which holds approximately one ton of ground phosphate. This hopper is fed by a "fines" elevator, which brings the ground phosphate from the large storage silo. Two valves control the flow of phosphate from the hopper to the scale. One controls the full stream until the

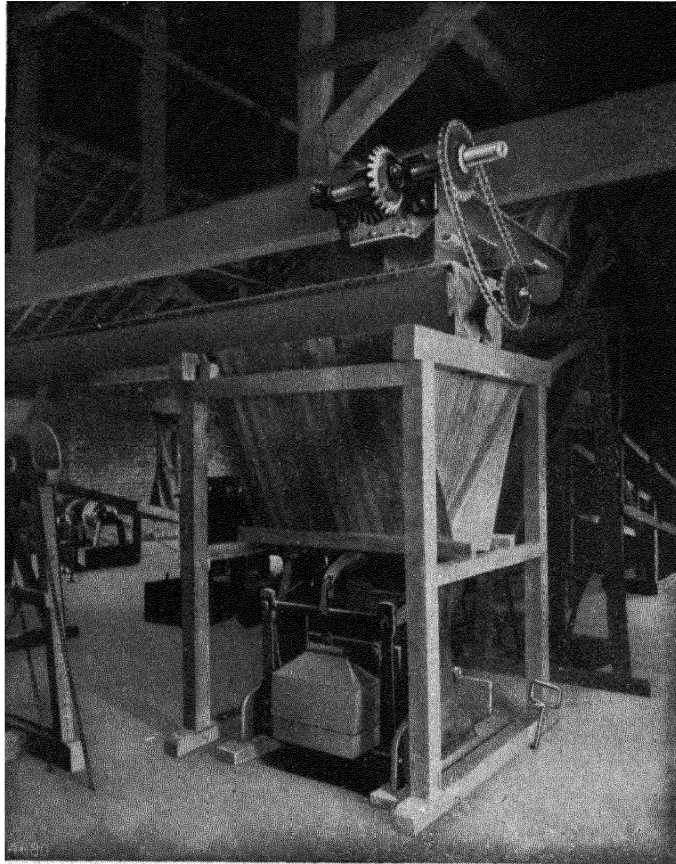


Fig. 29.—AUTOMATIC PHOSPHATE WEIGHER WITH FEED HOPPER

container is nearly full, when the second valve comes into operation and allows only a fine dribble to pass, which is immediately cut off when the scale balances. At the same instant the discharge valve is automatically opened, and the weighed charge of phosphate is emptied into a hopper immediately below. Three charges are held in this hopper, and then passed into the mixer. When the scale container has emptied, the discharge valve automatically closes and the inlet valve opens, and the operation commences again. There is a lever on the side of the apparatus to stop the discharge if it is not convenient to take the batch at the moment it is weighed.

The weighings are registered by a recording counter, so that it is possible to tell at any time the amount of phosphate that has passed through the scale. This machine, if properly fed from the hopper above, will weigh and discharge at the rate of 16 tons of ground phosphate per hour.

Weighing machines with automatic cut-offs have an advantage over hand-operated devices, in that the weights can be depended upon. There is no "hit or miss" closing of the valves at the correct moment, which is always liable to occur when operated by hand. There is accurate chemical control. Once the respective weights of acid and ground phosphate have been determined, the works chemist can depend upon the resultant mixture.

Superphosphate Mixers.—There are two types of superphosphate mixers in use to-day—vertical and horizontal. In Great Britain both types are in use, whereas in the United States of America mixers of the vertical type are used almost exclusively.

Vertical mixers are not all alike. The British pattern is mounted with one vertical shaft. The American pattern has usually two.

One of the simplest forms of vertical mixer is shown in Fig. 30. It consists of a cast-iron pot with an outlet opening in the bottom sealed with a plug-valve. The pot is covered with a dome-shaped casting, which carries one of the bearings for the vertical shaft. In this dome-shaped cover there are three openings. They are: (1) a rectangular opening for the ground phosphate to enter, (2) a 3-inch diameter opening for the acid pipe, and (3) a 9-inch square opening for the discharge of the toxic gases.

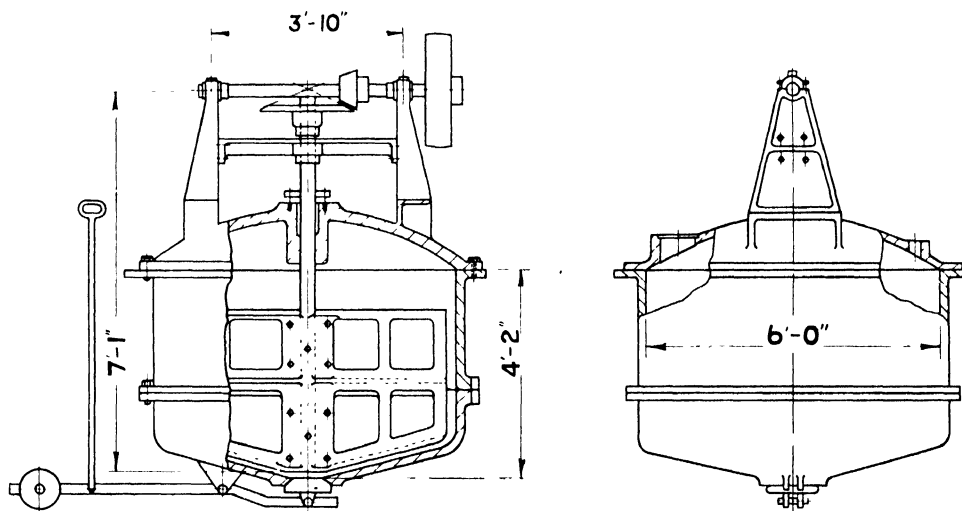


FIG. 30.—VERTICAL SUPER PHOSPHATE MIXER

The vertical shaft is made of wrought iron. Cast-iron gates, securely bolted together, grip the shaft. These act as stirrers, and mix the phosphate and acid together. The vertical shaft is driven through bevel gearing, and revolves at a speed of between 20 and 40 revolutions per minute.

The outlet valve is controlled by the hand lever, which projects through the floor above, and is within reach of the operator.

The operation is quite simple. The weighed or measured batches of phosphate and acid are passed into the mixer and are at once agitated by the stirrers, which continually revolve. After the lapse of a few minutes (because the chemical action takes place quickly), the operator lifts the vertical lever and opens the outlet valve, when the contents are quickly discharged into the den immediately below. The valve is closed, when the mixer is again ready for the next charge.

Another mixer of the vertical type is shown in Fig. 31, and is manufactured by R. Moritz of France. It is characterised by a special type of agitator. This comprises a series of inclined teeth, which cut the mass in two directions nearly perpendicularly. There are two points of discharge, so that a mixer of this type may serve two dens. It is designed to take a charge of approximately one ton. There are two outlets for the escape of gas, and these are connected direct with the dens, as shown in the illustration.

In the United States of America vertical mixers of the shallow type are generally used, and they are built to mix large batches. The pan is mounted on ball-bearings, and revolves at a suitable speed to enable the ploughs to stir and agitate the mass thoroughly.

Fig. 32 shows the standard type.

There are two stirrer shafts, working in opposite directions, on either side of the centre line, with the plug-opening in the centre.

The usual charge consists of approximately 3,700 lb. of rock and acid, and the mixer can be run regularly at the rate of from 15 to 18 mixes per hour.

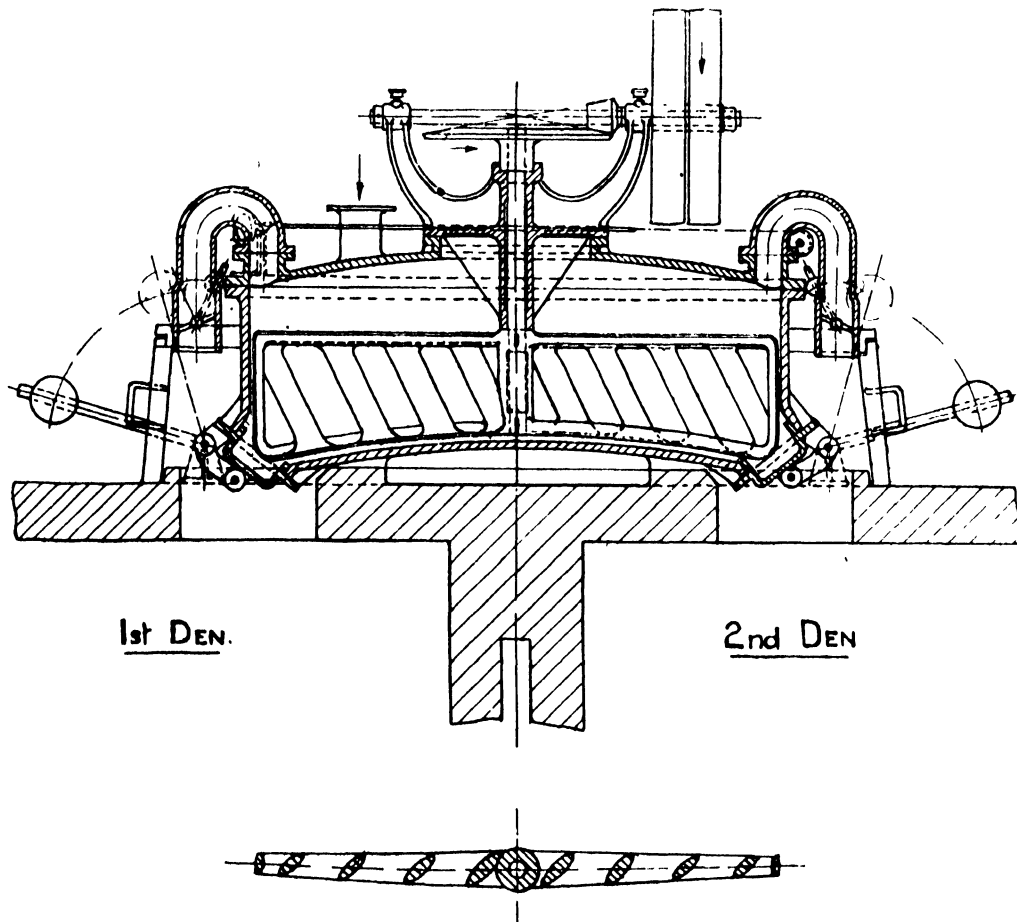


FIG. 31.—MORITZ VERTICAL MIXER

They are generally driven by a 15 h.p. electric motor, and the maintenance and repairs to the mixer amount to about £30 annually, (1938).

In the United States of America they estimate the life of the mixing equipment, including dust and acid scales, hoppers, etc., at fifteen years.

These machines are of very heavy design, as in the larger works one of these mixers may have to produce approximately 300 to 400 tons of superphosphate per day.

In some of the American works two of these mixers are mounted on a movable platform, which also supports two phosphate scales and two acid measurers, as shown in Fig. 33. This platform travels over a series of fixed vertical dens, each holding 200 to 300 tons, and makes its own seal with any of them. This system of mixing is confined to America, and particularly to the largest works, where the outputs range from 500 to 1,000 tons per day of twenty-four hours.

Horizontal mixers have been in use for some considerable time. A modern type is illustrated in Fig. 34. It consists of a cylindrical drum supported on trunnion bearings, and is free to revolve. An opening is provided along two-thirds of its length for charging and discharging. A cast-iron shaft passes through the centre of the drum, on which are mounted a series of stirrers, which continually revolve whilst the process of mixing is proceeding. The charge of phosphate and acid is passed into the mixer, the drum is then slowly rotated, when the contents are discharged into the den. To enable the operator to watch the rotation of the mixer drum, and stop it when the inlet opening is central with the feeding chute, a tell-tale indicator is situated on the mixer floor. The combined charge is 12 to 16 cwt. of phosphate and acid.

Chemical Aspect

Having completed the treatment of the purely mechanical aspect of mixing plants, it will be appropriate now to deal with the chemical aspect, relating to this operation. The first consideration

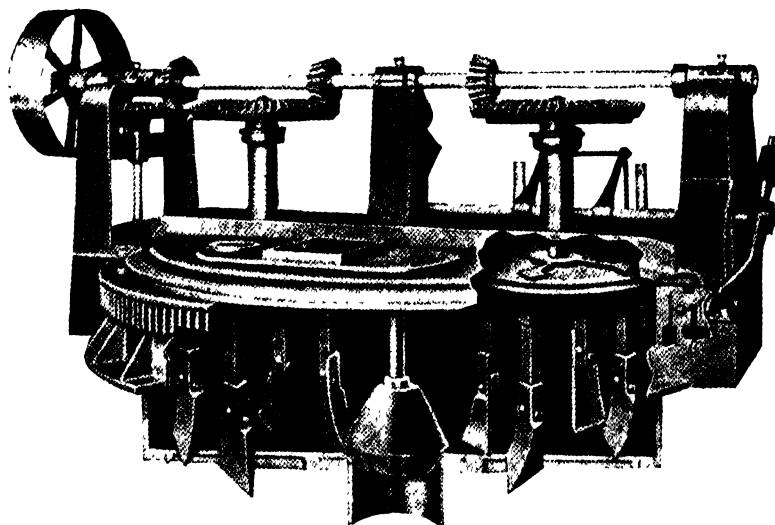


FIG. 32.—STANDARD TYPE OF MIXER USED IN THE U.S.A.

which arises is, what quantity of acid must be used per unit weight of ground rock phosphate if a satisfactory product is to be obtained, having a maximum water-soluble phosphate content, together with the other requisite physical properties which a good superphosphate should possess?

It is pointed out later in this chapter that a trial-and-error method is sometimes adopted in order to determine the proportions of sulphuric acid and ground phosphate for a given batch.

Whatever may be the merits of such a method, experience has revealed the need initially for the acid requirements to be computed on the basis of the analysis of the raw phosphate.

After a trial mixing has been effected, based on the proportions afforded by such a computation, the product should be allowed to mature. This only involves a duration of a few days, if adequate time contact has been given in the mixing plant and the mixing has been efficient.

Subsequently, a determination of the moisture, water-soluble and water-insoluble phosphates, and free phosphoric acid contents, should be made, and dependent on these results the acid required should be adjusted, to ensure the best possible product, when regarded from the chemical and physical points of view.

It must be recalled that raw phosphates vary very appreciably, not alone as regards physical characteristics, but in point of chemical composition.

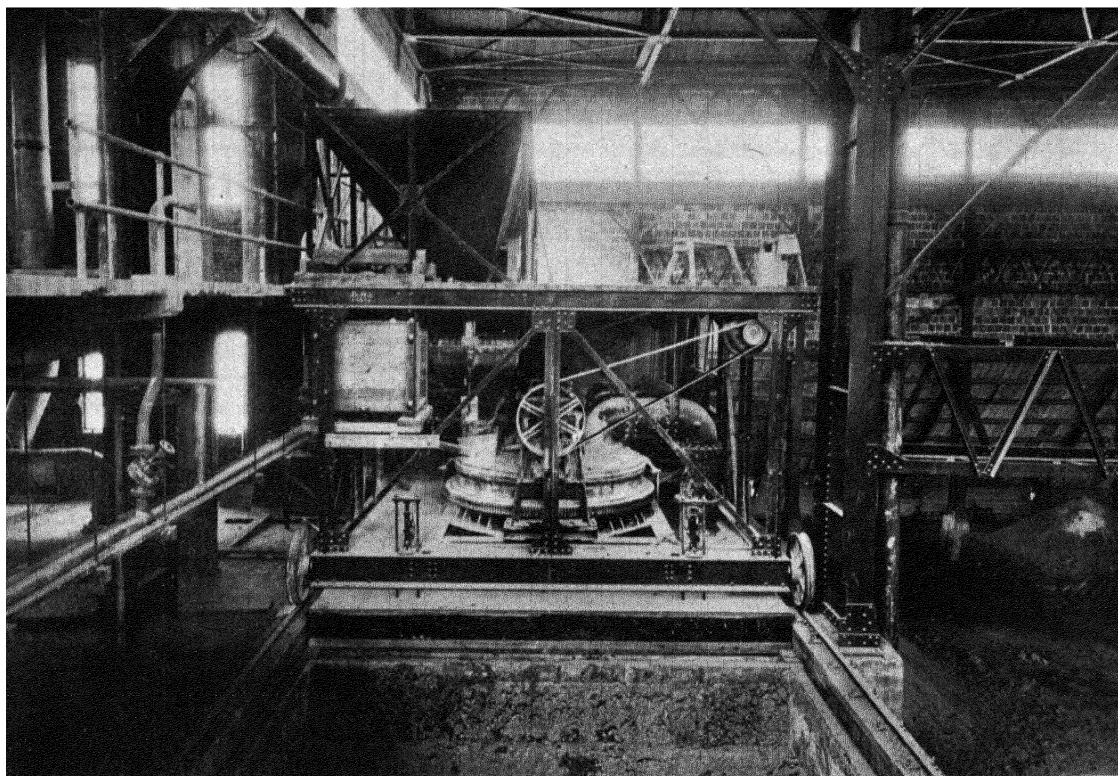


FIG. 33.—MIXER MOUNTED ON A MOVABLE PLATFORM

Obviously, one must know the principal constituents of the rock phosphate which it is intended to use before one can compute the amount of acid which will be required per unit weight of phosphate employed.

Given an analysis of the principal constituents, it is not a difficult matter to calculate the quantity of sulphuric acid, of varying specific gravities and temperatures, which will be required for admixture with a unit weight of phosphate rock.

The following tables, it is hoped, will be found of use in admitting of a ready determination of the weight of acid required for a raw phosphate of a given analysis.

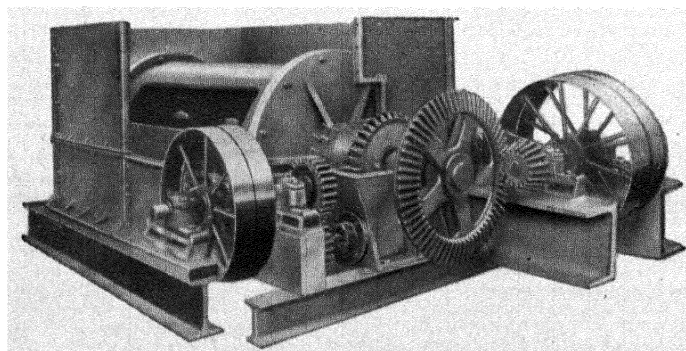


FIG. 34.—SULLIVAN HORIZONTAL MIXER

Table 14, which is subjoined, relates to the quantity of sulphuric acid, of strengths ranging from 106° Tw. (50° Bé.) to 122° Tw. (54·7° Bé.), and of temperatures ranging from 15·5° C. (60° F.) to 60° C. (140° F.), required per unit weight of tricalcium phosphate.

Tables 15, 16 and 17 similarly deal with the calcium carbonate, iron and alumina, and calcium fluoride and sodium chloride contents of raw mineral phosphate, and furnish the acid equivalent per unit weight of the several constituents.

Tables showing the quantity in pounds, of sulphuric acid of various strengths and temperatures, required for every pound of the following substances in 100 lb. of phosphate rock :

- (i) Tricalcium phosphate.
- (ii) Calcium carbonate.
- (iii) Iron and aluminium oxides.
- (iv) Calcium fluoride and sodium chloride.

TABLE 16
Tricalcium Phosphate

Temperature.		Density in Degrees Twaddell and Baumé.								
° F.	° C.	106 Tw. 50·0 B.	108 Tw. 50·6 B.	110 Tw. 51·2 B.	112 Tw. 51·8 B.	114 Tw. 52·4 B.	116 Tw. 53·0 B.	118 Tw. 53·6 B.	120 Tw. 54·1 B.	122 Tw. 54·7 B.
60	15·5	1·010	0·996	0·983	0·970	0·957	0·945	0·932	0·920	0·908
70	21·1	1·003	0·990	0·977	0·963	0·951	0·938	0·926	0·914	0·902
80	26·6	0·996	0·983	0·970	0·957	0·945	0·932	0·920	0·908	0·897
90	32·2	0·990	0·977	0·963	0·951	0·938	0·926	0·914	0·902	0·892
100	37·7	0·983	0·970	0·957	0·945	0·932	0·920	0·908	0·897	0·887
110	43·3	0·977	0·963	0·951	0·938	0·926	0·914	0·902	0·892	0·882
120	48·8	0·970	0·957	0·945	0·932	0·920	0·908	0·897	0·887	0·877
130	54·4	0·963	0·951	0·938	0·926	0·914	0·902	0·892	0·882	0·872
140	60·0	0·957	0·945	0·932	0·920	0·908	0·897	0·887	0·877	0·868

TABLE 17
Calcium Carbonate

Temperature.		Density in Degrees Twaddell and Baumé.								
° F.	° C.	106 Tw. 50·0 B.	108 Tw. 50·6 B.	110 Tw. 51·2 B.	112 Tw. 51·8 B.	114 Tw. 52·4 B.	116 Tw. 53·0 B.	118 Tw. 53·6 B.	120 Tw. 54·1 B.	122 Tw. 54·7 B.
60	15·5	1·56	1·54	1·52	1·50	1·48	1·46	1·445	1·43	1·41
70	21·1	1·55	1·53	1·51	1·49	1·47	1·45	1·44	1·42	1·40
80	26·6	1·54	1·52	1·50	1·48	1·46	1·445	1·43	1·41	1·39
90	32·2	1·53	1·51	1·49	1·47	1·45	1·44	1·42	1·40	1·385
100	37·7	1·52	1·50	1·48	1·46	1·445	1·43	1·41	1·39	1·38
110	43·3	1·51	1·49	1·47	1·45	1·44	1·42	1·40	1·385	1·37
120	48·8	1·50	1·48	1·46	1·445	1·43	1·41	1·39	1·38	1·36
130	54·4	1·49	1·47	1·45	1·44	1·42	1·40	1·385	1·37	1·35
140	60·0	1·48	1·46	1·445	1·43	1·41	1·39	1·38	1·36	1·345

TABLE 18

Iron and Aluminium Oxides

Temperature.		Density in Degrees Twaddell and Beaumé.								
° F.	° C.	106 Tw. 50.0 B.	108 Tw. 50.6 B.	110 Tw. 51.2 B.	112 Tw. 51.8 B.	114 Tw. 52.4 B.	116 Tw. 53.0 B.	118 Tw. 53.6 B.	120 Tw. 54.1 B.	122 Tw. 54.7 B.
60	15.5	3.58	3.53	3.49	3.44	3.39	3.35	3.30	3.26	3.22
70	21.1	3.56	3.51	3.47	3.42	3.37	3.32	3.28	3.24	3.20
80	26.6	3.53	3.49	3.44	3.39	3.35	3.30	3.26	3.22	3.18
90	32.2	3.51	3.47	3.42	3.37	3.32	3.28	3.24	3.20	3.15
100	37.7	3.49	3.44	3.39	3.35	3.30	3.26	3.22	3.18	3.13
110	43.3	3.47	3.42	3.37	3.32	3.28	3.24	3.20	3.15	3.11
120	48.8	3.44	3.39	3.35	3.30	3.26	3.22	3.18	3.13	3.09
130	54.4	3.42	3.37	3.32	3.28	3.24	3.20	3.15	3.11	3.07
140	60.0	3.39	3.35	3.30	3.26	3.22	3.18	3.13	3.09	3.04

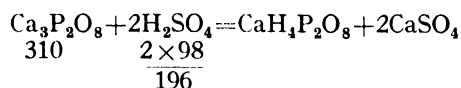
TABLE 19

Calcium Fluoride and Sodium Chloride

Temperature.		Density in Degrees Twaddell and Beaumé.								
° F.	° C.	106 Tw. 50.0 B.	108 Tw. 50.6 B.	110 Tw. 51.2 B.	112 Tw. 51.8 B.	114 Tw. 52.4 B.	116 Tw. 53.0 B.	118 Tw. 53.6 B.	120 Tw. 54.1 B.	122 Tw. 54.7 B.
60	15.5	2.29	2.27	2.24	2.20	2.17	2.14	2.11	2.08	2.06
70	21.1	2.28	2.25	2.22	2.19	2.16	2.13	2.10	2.07	2.05
80	26.6	2.27	2.24	2.20	2.17	2.14	2.11	2.08	2.06	2.03
90	32.2	2.25	2.22	2.19	2.16	2.13	2.10	2.07	2.05	2.02
100	37.7	2.24	2.20	2.17	2.14	2.11	2.08	2.06	2.03	2.01
110	43.3	2.22	2.19	2.16	2.13	2.10	2.07	2.05	2.02	1.99
120	48.8	2.20	2.17	2.14	2.11	2.08	2.06	2.03	2.01	1.97
130	54.4	2.19	2.16	2.13	2.10	2.07	2.05	2.02	1.99	1.95
140	60.0	2.17	2.14	2.11	2.08	2.06	2.03	2.01	1.97	1.94

Explanation of the Tables

I. One molecule of tricalcium phosphate absorbs two molecules of sulphuric acid, according to the following equation :



Therefore 196 lb. of monohydrate sulphuric acid will be required for 310 lb. of tricalcium phosphate, or 1 lb. of phosphate will require

$$\frac{196}{310} = 0.633 \text{ lb. of acid.}$$

Sulphuric acid of 112° Tw. density at 60° F. contains 65.2 per cent of monohydrate acid, so that the quantity of acid of this strength that will be required is

$$\frac{0.633 \times 100}{65.2} = 0.97 \text{ lb.}$$

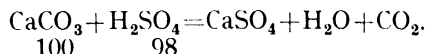
Since the temperature of the acid affects its density, it is necessary to take this into account when making these calculations. For example, acid of 112° Tw. at 110° F. is equivalent to acid of 117° Tw. at 60° F., because over this particular range the density decreases 1° Tw. for every 10° F. rise in temperature.

Acid of 117° Tw. at 110° F. contains 67.4 per cent H_2SO_4 .

Therefore $\frac{0.633 \times 100}{67.4} = 0.938$ lb. of acid of this density and temperature will be required for every lb. of tricalcium phosphate.

Table 16 shows these quantities for any density between 106° and 122° Tw., and for any temperature between 60° F. and 140° F.

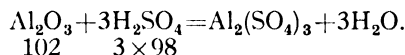
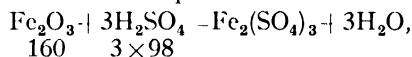
II. Similar data for calcium carbonate are given in Table 17. Sulphuric acid reacts with calcium carbonate to form calcium sulphate, water, and carbon dioxide. Thus :



From the molecular weights it will be seen that 0.98 lb. of monohydrate acid is required for 1 lb. of calcium carbonate. Assuming that acid of 112° Tw. at 110° F. were used, then the quantity would be

$$\frac{0.98 \times 100}{67.4} = 1.45 \text{ lb.}$$

III. Table 18 is based on the assumption that iron and aluminium oxides occur in equal proportions, and that the following reactions take place :

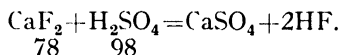
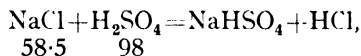


Therefore $\frac{160+102}{2} = 131$ lb. of these oxides would absorb $3 \times 98 = 294$ lb. of monohydrate sulphuric acid, or 1 lb. would require $\frac{294}{131} = 2.24$ lb.

Using the same example as in the previous calculations, i.e. acid of 112° Tw. at 110° F., then

$$\frac{2.24 \times 100}{67.4} = 3.32 \text{ lb.}$$

IV. Table 19 shows the quantity of acid absorbed in decomposing calcium fluoride and sodium chloride. Since these compounds usually occur only in comparatively small amounts, it is assumed that they exist in equal proportions. The following calculation shows the basis of the figures :



$$(1) \frac{58.5+78}{2} = 68.25.$$

(2) $\frac{98}{68.25} = 1.436$ lb. monohydrate sulphuric acid per lb. of an equal mixture of calcium fluoride and sodium chloride.

$$(3) \frac{1.436 \times 100}{67.4} = 2.13 \text{ lb. of 112° Tw. acid at 110° F.}$$

An example of the application of the foregoing tables to a typical mineral phosphate is given below. Its usefulness does not need to be urged.

TABLE 20

Gafsa phosphate.	Percentage.	Acid of 114° Tw. at 100° F.
Calcium phosphate	59.44	$\times 0.932 = 55.39$
Calcium carbonate	11.95	$\times 1.445 = 17.265$
Iron oxide and alumina	1.68	$\times 3.3 = 5.544$
Calcium fluoride and salt	5.10	$\times 2.11 = 10.76$
		88.959
Magnesium (Mg.)	5.80	(say) 2.900
		91.859

representing the lb. of sulphuric acid of 114° Tw. at 100° F. required per 100 lb. of Gafsa phosphate.

Actually, the fertiliser manufacturer, No. 16E, Table 21, used 92.5 parts of acid of the strength and temperature named, per 100 parts of the said Gafsa phosphate.

This indicates how closely the calculated figure can approach the one which continued practical working reveals to be the best from the standpoints of physical and chemical suitability.

Our experience has brought us into touch with many fertiliser works, where we have had an opportunity of investigating working conditions and peculiarities of practice. The following table (21) represents the mixing details at various works, and is additionally helpful in that, in most cases, the fineness of the raw phosphate, the temperature and strength of the acid used, the type of den, whether slicing is effected or not, particulars of how the samples were drawn, and the analysis in terms of moisture, total P_2O_5 , water-soluble and water-insoluble phosphates, and free acid are all indicated.

Practical notes relating to mixing, and control of this unit process

There is still a consensus of opinion, as has already been observed, that trial mixings on a definite works scale are essential to a correct determination of the nature of the mixing.

That these trials would be more valuable if they were correlated from several points of view is generally conceded. Complete screening tests of the phosphate rock, so as to give some definite indication of the particle size, with strengths and temperatures of the acid used, together with a continuous record of the temperature of the gases evolved immediately above the mass in the den, with particulars relating to the rate at which the product matures (involving, as it does, an analysis of the free acid, water-soluble and water-insoluble phosphates, and water contents of the material immediately it is discharged from the den, and then each twenty-four hours afterwards, until something approaching a constancy of composition is reached), when correlated, would furnish information of inestimable advantage.

It should be remarked here that it is always advisable so to regulate the "mixing" as to leave a little calcium phosphate unattacked. This means a certain loss of efficiency, and newer methods may impose a modification of this view.

The above method is recommended. It may appear an onerous job, but it is certain that the possession of such data would be of material service in tracing subsequent dislocation in manufacture.

Although applicable to many varieties of phosphates, such a method would be useless with certain mineral phosphates, especially some of the apatite variety, because the operation is sluggish, the mass becomes pasty, the acid attracts moisture, and this enfeebles the reaction. Nothing but an unsatisfactory quality of superphosphate can result.

With such raw materials it is essential that another type of procedure should be pursued. Some indication of the behaviour of such a mineral phosphate can be afforded by treating the phosphate with sulphuric acid in a suitable vessel with carefully regulated stirring, which must be *less* rather than *more* than that actually given in normal practice. The vessel containing the mass should be allowed to stand for twenty to thirty hours in a warm place. It must be hermetically sealed.

Dependent on the condition of the mixture after the elapse of the time named, a judgment can be formed as to what may be anticipated in actual practice. If, for example, the mixture is in a reasonably dry condition, it can usually be concluded that solidification and drying will be better on a large scale.

It is necessary to exceed the calculated quantity of sulphuric acid with fluoride phosphates. This has been emphasised by the treatment of Kola phosphate—an apatite—and what has been demonstrated is that the complete decomposition of the apatite takes months.

Generally speaking, the richer the raw material is in tricalcium phosphate the less should be the excess quantity of acid used, as in the absence of iron oxide and alumina, or silicates, there is little prospect of any extraneous body absorbing the excess acid.

Raw phosphates which are damp or moist, as indeed those which are difficult of attack, require stronger acid than those which are dry and rich in calcium carbonate. Somme and Algerian phosphates are rich in calcium carbonate and hence require more acid. But it is unusual to employ a greater excess than 5 per cent of the computed quantity. Phosphates such as the last named, rich in carbonate, are best worked with cold acid, whereas those which are poor in carbonate should be treated with hot acid.

The preservation of water-soluble phosphate in superphosphates appears to be dependent in some degree on the strength of the acid used. At all events, sulphuric acid of 120° Tw. appears to contribute to optimum preservation, whereas a certain instability is noted with acid of 106° Tw.

It must not be assumed that all the tricalcium phosphate in mineral phosphates is rendered completely soluble by the action of sulphuric acid. Such a hypothesis cannot be supported by actual experience. There is always a certain amount of insoluble phosphate present, and the extent of this depends on many factors, not the least of which is the quality of the raw phosphate used. The sensible extent to which iron oxide and alumina absorb acid is strikingly shown in Table 18 (p. 70). Little wonder that superphosphate manufacturers are averse from raw phosphates containing any appreciable percentage of these constituents. Apart from this, there are other reasons for discouraging the use of a raw phosphate having an undue content of iron oxide or alumina. This aspect is suitably treated under reversion.

Formerly, one advised that the dens should not be filled brim full, but should allow of a vacant space at the top as a means of regulating the toxic gases which are withdrawn under suction. With modern dens this practice still obtains. The decomposition of the phosphate takes place partially in the mixer, but is completed in the den, and occasional agitation of the mass there, and the use of heated air for drying, may be a step in the right direction. With cold acid the reaction is sluggish, whereas with hot acid it is conceivable that the mass may thicken too readily. Any such condition can, of course, be avoided in subsequent mixings by using a more dilute acid.

The rapidity with which carbon dioxide is disengaged causes effervescence, and temperatures in the mass ranging from 110° to 140° C. are reached. The mass settles in the den slowly. To maintain its mobility hitherto calcium carbonate and a little magnesium carbonate were used. In this way greater quantities of water were evaporated, besides which, due to the formation of crystallised magnesium sulphate, an additional desiccating action resulted. It is certainly contrary to modern practice to use dryers in the den. Advantage should be taken of the available heat of reaction for the evaporation of all unnecessary water.

The temperature of the mass within the den, or autoclave, is a function of the pressure obtaining, and the degree to which heat is conserved. The duration of mixing is a matter of importance. This has been revealed by the introduction of the Broadfield process, where the mixer is of a unique kind, and where the duration of mixing is appreciably longer than has hitherto been regarded as necessary in this country.

TABLE 21

Works.	Phosphate used.	Weight of phosphate.	Fineness.	Weight of acid.	Bé.	Tw.	Temp. °C.	Temp. °F.	Type of den.	If sliced.	Moisture.	Total P ₂ O ₅ .	Sol.	In-sol.	Free acid as P ₂ O ₅ .	Sample taken.
No.											%	%	%	%		
1 F.	M'Dilla	672 lb.	50%+100	585 lb.	53	116	—	—	Milch	No	—	14.65	13.74	0.91	—	As cut out.
2 W.	Tunisian	672 lb.	—	585 lb.	52.4	114	—	—	Sturtevant	Yes	15.8	16.69	13.79	2.9	2.10	
3 W.	Florida pebble	672 lb.	—	672 lb.	52.4	114	—	—	"	"	15.6	17.08	15.57	1.51	7.00	
4 N.	Florida pebble	672 lb.	20%+100	630 lb.	51.8	112	37.7	100	"	"	—	17.99	17.04	0.95	—	
5 B.	Constantine	300 kg.	20%+100	255 kg.	53	116	15	60	"	"	15.04	16.38	14.59	1.79	6.59	
6 C.	Florida	672 lb.	8%+60	620 lb.	50	106	51.6	125	"	No	12.60	18.74	17.08	1.66	3.64	Tested two days after.
7 A.	"	630 lb.	8%+60	562 lb.	51.3	110	48.8	120	Svenska	Yes	12.0	18.73	16.98	1.75	4.00	
8 D.B.	"	1200 lb.	3%+100	1050 lb.	53	116	48.8	120	Crane excavatingden	No	12.0	—	—	0.75	6.00	
9 L.Z.	"	300 kg.	30%+100	285 kg.	52	112.6	Atmosphere	—	Wenk	"	13.6	19.56	17.62	1.94	6.39	Same day.
10 L.Z.	"	300 kg.	20%+100	285 kg.	51	109.2	"	"	"	"	15.4	17.84	16.81	1.03	8.66	"
11 L.Z.	"	300 kg.	20%+100	270 kg.	52	112.6	"	"	"	"	13.2	19.06	17.75	1.31	6.39	"
12 L.Z.	Morocco	300 kg.	20%+100	285 kg.	53	116	"	"	"	"	11.52	19.07	18.60	0.47	6.39	"
13 C.	"	390 kg.	25%+80	385 kg.	53	—	25	—	Sturtevant	Yes	13.65	18.25	17.45	0.8	8.09	"
14 N.	Constantine	672 lb.	20%+100	652 lb.	53.6	118	—	—	"	"	12.5	18.53	16.65	1.88	5.3	As cut out.
15 V.	Gafsa, 58-63%	672 lb.	20%+100	616 lb.	52.7	115	43.3	110	"	"	16.0	14.50	13.50	1.00	3.67	"
16 E.	Gafsa, 59%	10 cwt.	20%+100	94 cwt.	52.4	114	37.7	100	"	"	18.0	15.91	13.68	2.23	4.00	"
17 A.	Florida	672 lb.	8%+60	594 lb.	53	116	59.0	138	"	"	—	19.23	18.62	0.61	Trace	Two weeks old.

All new processes stress the necessity for longer time contact and completion of the essential reactions occurring in the decomposition of phosphate rock. But the modern Nordengren process (page 90) disturbs this conception, because the time factor in the mixer is 2 to 5 seconds, in the solidifying vessel 5 to 20 minutes and in the chamber 1 to 3 hours.

The method of grinding, and the relative proportions of fine powder to coarse material, obviously influence the conversion of tricalcium phosphate to the water-soluble form. A too great fineness leads to an unsatisfactory physical condition in the final product. It must be remembered that a certain granular structure is necessary for acid penetration. Raw phosphate which is too coarse cannot be attacked satisfactorily by the acid, and it will be found that there is much water-insoluble phosphate.

With the improved systems of grinding and mixing which have been introduced during the last few years, it is possible to reduce the insoluble calcium phosphate to 0.5—0.7 per cent. Prior to the introduction of these new systems, it was not uncommon for one to find as much as 2 per cent of insoluble tricalcium phosphate, $\text{Ca}_3\text{P}_2\text{O}_8$.

Endeavours to produce water-soluble phosphate by the action of a mixture of sulphuric acid and hydrochloric acid and raw phosphates have been made, but the presence of free hydrochloric acid was not only a disability from the point of view of attack on the bags, but corrosion of metallic parts was another collateral defect. Moreover, it must be remembered that hydrochloric acid is much more expensive than sulphuric acid.

Commercial Calcium Superphosphate

This product is manufactured and sold in various grades containing from 10 to 21 per cent of phosphoric acid (P_2O_5), dependent on the quality of the rock phosphate employed. Generally speaking, the water-soluble phosphoric acid content of superphosphate is rather more than 50 per cent of the insoluble phosphoric acid content of the phosphate rock from which it is derived. Where the combined oxides of iron and alumina exceed say 1.5 per cent, reversion of some of the water-soluble phosphoric acid will occur, and the foregoing statement will need to be qualified.

The sale of fertiliser products is controlled in Great Britain under the Fertiliser and Foodstuffs Act passed in 1926, and Statutory Rules and Orders, 1932, No. 658. It is true to say that practically all the countries of the world have similar legislation: practice varies regarding the solubility guaranteed.

Water-solubility only is the basis in some countries, whereas water and citrate solubility constitute the bases of sales in other countries (see list below).

Solubility Guaranteed.	
Water-solubility.	Water and citrate-solubility.
Austria, Belgium, Czechoslovakia, Denmark, Finland, Germany, Great Britain, Holland, Hungary, Jugoslavia, Latvia, Norway, Poland, Switzerland, South Africa, India, Ceylon, Japan, Australia and New Zealand.	Estonia, France, Greece, Italy, Portugal, Roumania, Spain, Sweden, United States and North Africa.

What is known as 30 per cent superphosphate is a fertiliser containing 30 per cent of phosphate calculated as tribasic phosphate, which has been rendered by treatment soluble in water. Citrate-soluble and insoluble are excluded by English practice. A 30 per cent superphosphate would contain the following equivalents:

- (a) 30 per cent, expressed as $\text{Ca}_3\text{P}_2\text{O}_8$
- (b) 22.6 per cent, expressed as $\text{CaH}_4\text{P}_2\text{O}_8$
- (c) 13.74 per cent, expressed as P_2O_5

The molecular weights of the three foregoing are :

(a)	$\text{Ca}_3\text{P}_2\text{O}_8$.	.	.	310.234
(b)	$\text{CaH}_4\text{P}_2\text{O}_8$.	.	.	234.0852
(c)	P_2O_5	.	.	.	141.964

Therefore, the factors for the conversion of P_2O_5 and $\text{CaH}_4\text{P}_2\text{O}_8$ to tribasic phosphate, $\text{Ca}_3\text{P}_2\text{O}_8$ are respectively 2.185 and 1.326.

Calcium superphosphate which has been carefully prepared should not contain more than 10 per cent of water : in fact, 8 per cent would be preferable, and possibly 4 per cent will be the content in granulated superphosphate. Dicalcium phosphate should never be absent—indeed, the quantity of the last-named compound should be approximately equal to the free phosphoric acid present in the superphosphate. The mono- and dicalcium phosphates should largely exist in the hydrated form, and the calcium sulphate should exist largely as such. The presence of any hemihydrate or dihydrate is indicative of old material, or represents “super” prepared with insufficient sulphuric acid.

Ideas concerning what superphosphate should be are changing. In the near future, perhaps any superphosphate which yields to light pressure between the fingers will be regarded as of unsatisfactory condition. Conceivably, farmers and others will look for a hard granule, ranging from 1.5 to 4 mm. in size, and will call for uniformity of size, within limits. At all events, this predicts the direction in which advance of technique and improved requirements are inevitably leading us.

CHAPTER VI

MECHANICAL DENS AND EXCAVATORS—BATCH TYPE

ONE of the first mechanical dens of this type to be invented was known as the “*Wenk*”; this den is still very popular in France, where many are in use. It consists of a brick encasement built in the form of a horizontal cylinder, which gives to the apparatus the desired stability, and enables it to be lined internally with acid-proof lining, or to be constructed of any material having the required resistance. Along the bottom of the den there is a slot-opening, between the rails on which the excavator carriage travels.

Fig. 35 shows two “*Wenk*” dens side by side with one common mixer. There is an opening near the top of the den in the centre of the length, which admits the liquid mixture. The opening along the bottom is closed when the den is being charged. The end of the den adjacent to the excavator is sealed with a door, which is lifted up out of the way when the mass is ready to be cut out.

The apparatus for the mechanical discharging of the den consists of a carriage on which is mounted the cutter. This is illustrated in Fig. 36. An electric motor is situated on top of the carriage framework and gives motion to the cutter, which runs at 22 revolutions per minute: this same motor, through a system of gearing, also propels the carriage along the den in such a manner that the forward motion of the cutter into the superphosphate is sufficiently slow to reduce it to a powder, owing to the fineness of the cut. The rate of travel is approximately $1\frac{3}{4}$ inches per minute. On reaching the end of its travel the carriage is automatically stopped, and the return is effected at a high speed.

The cutter is composed of a series of knives fixed to the carriage in the form of a cross (see Fig. 37). The extreme edges of the knives, in the form of paws, are slightly bent in the direction of rotation of the cutter. Immediately behind the cutter a stationary wrought-iron disc is fixed to the carriage, which prevents the superphosphate, during the process of cutting, from falling on to the carriage, motor, and gearing, and also prevents the escape of acid vapours from the den itself.

Immediately below the den, and central with the longitudinal opening, there is situated a tray conveyor. As the superphosphate is shaved off the block by the action of the cutter, it falls through the opening in the bottom of the den on to the tray conveyor and thence to a superphosphate elevator.

When two dens are placed side by side, as shown in Fig. 35, one excavator carriage serves the two. It is then arranged with an under-carriage which moves on a track at right angles to the axes of the dens. With this arrangement, one den is being charged whilst the mass is being cut out of the other.

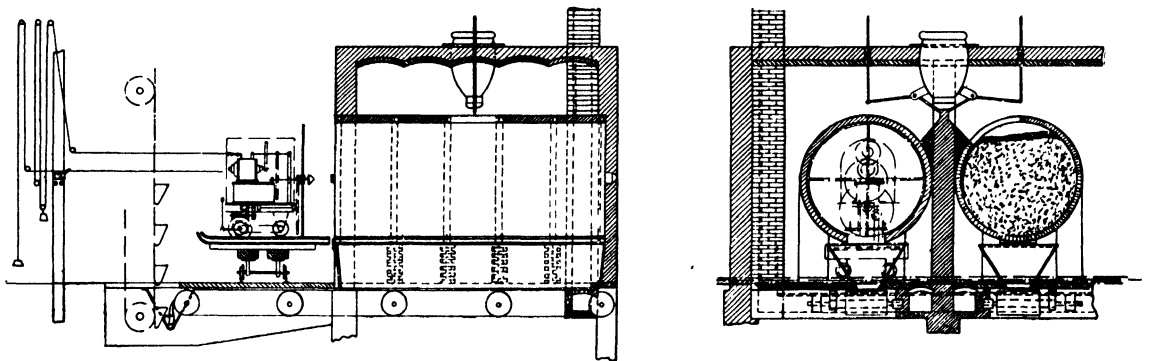


FIG. 35.—WENK MECHANICAL DEN

A "Wenk" den 3 metres in diameter and 6 metres long has a capacity of approximately 40 tons, it takes two hours, twenty minutes to cut out the mass, and the power required to operate the cutter and carriage is approximately 10 b.h.p.

The "Milch" den operates in a reverse manner to the "Wenk."

In this apparatus the excavator is stationary, and the den, which is a steel cylinder constructed like a boiler shell and mounted on wheels, travels forward on to the excavator.

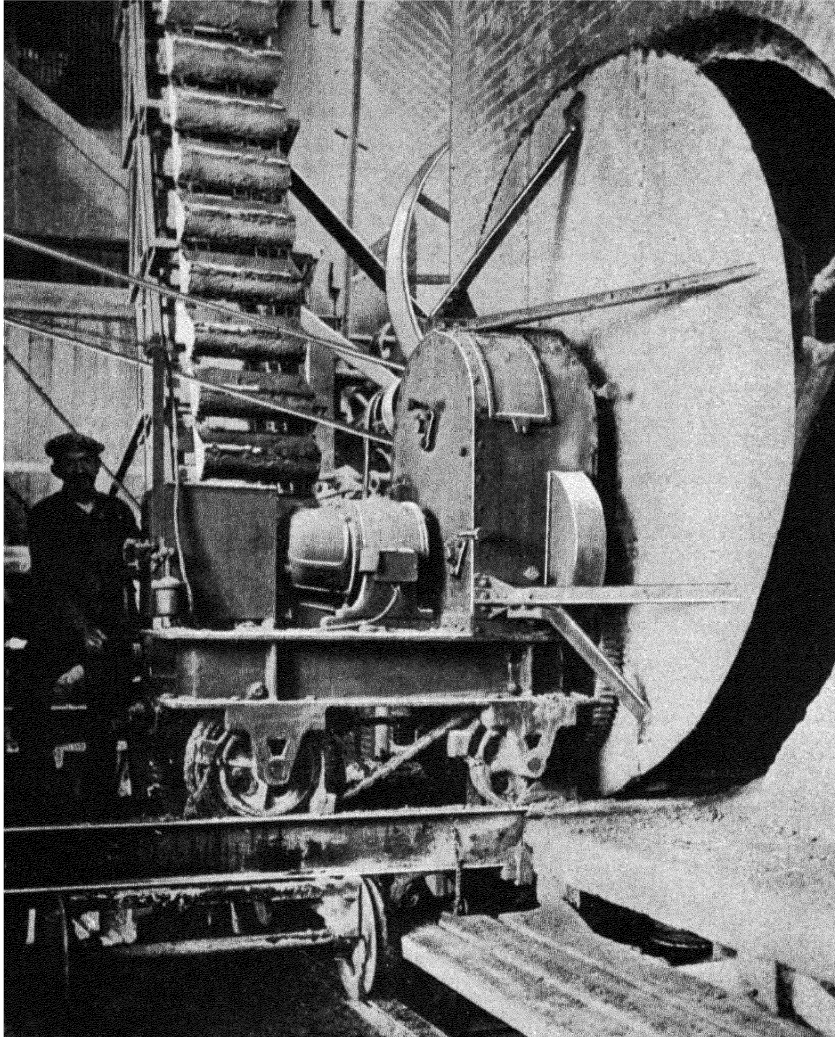


FIG. 36 APPARATUS FOR MECHANICAL DISCHARGE OF WENK DEN

Fig. 38 shows a "Milch" den at the commencement of its forward movement.

The travel is controlled by two heavy screws attached to the cylinder, one on either side. The driving gear is on the extreme right, and is so arranged that the den travels forward at a slow speed and travels back at an accelerated rate.

Along the bottom of the den there is a series of hinged doors, which are opened when the charge is ready to be cut out. As the cylinder works out to the cutter, the superphosphate is shaved off and falls through the opening in the bottom of the cylinder on to a conveyor, which removes it to the store.

When the whole of the charge of superphosphate is cut out, the machinery is reversed, and the cylinder returned to the mixing chamber. The end door is dropped into position and clamped, and the bottom doors are sealed, when the den is ready for the next charge.

These dens are usually built to hold from 30 to 60 tons of superphosphate. Very little power is required to operate them, and one man only is necessary to attend to the running of the machinery.

The "Sturtevant" den is illustrated in Fig. 39 and consists of a large box-like structure. The bottom and one end wall are fixed, and constructed of concrete or brickwork. The two side walls and the top, which are made of timber, are mounted on a steel chassis which runs on rails at either side. The excavator is also mounted on the chassis, and travels with the den.

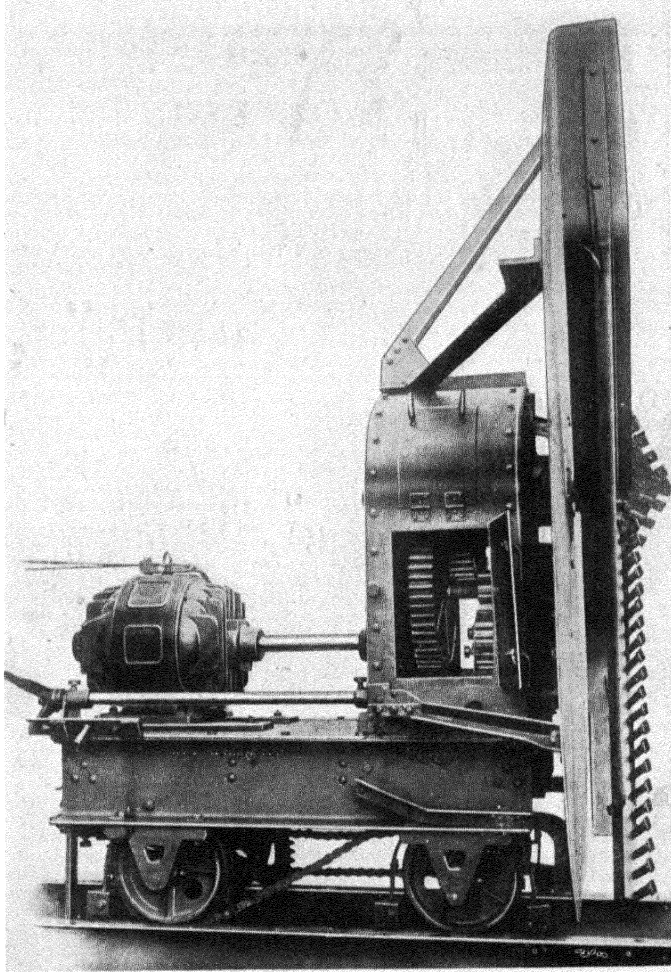


FIG. 37.—CUTTER USED IN THE WENK DEN

The movable end wall (nearest the excavator) is hoisted up clear of the den, when the excavating operation commences: it is raised or lowered by a winch and is counterbalanced. The sides of the den are hinged to the chassis at the top and held against the concrete base by a series of clamps and wedges. The weight of the massive block of superphosphate is not carried on any portion of the movable structure, thus reducing to a minimum the power required for traversing.

The back of the den is formed of reinforced concrete and built up to within 12 inches of the top of the movable chassis, which allows the gas evolved during mixing to be withdrawn by a fan into a specially constructed fume duct, and pass thence to the condenser.

On the top of the den there is a cast-iron angle flange, which makes a joint with a corresponding flange on the mixer hopper. The act of moving the chassis into position makes a tight joint between these flanges.

The motor for driving the excavator is fixed on top of the movable chassis, and the whole traverses backwards and forwards by a system of racks and worm gears. The racks and worm gears are placed on each side of the framework, and driven by a common transverse shaft which gives an even movement to the carriage.

The excavator consists of six vertical scoops carrying knives mounted on spiders, which are keyed on to a vertical shaft.

The method of operation is as follows:

Charging.—As illustrated in Fig. 39, the movable carriage is traversed until the end wall A presses against the concrete block B. Coincident with this, chute C on top of the den is sealed against the one marked D on the fixed hopper E. The swinging sides of the den F are next pressed into position against the sides of the concrete block B by a simple arrangement of wedges: the movable end wall G is also lowered into position and securely held by its system of wedges. The

den is thus sealed and ready to receive its charge from the mixer. The time of charging varies from three-quarters of an hour to two hours, according to the capacity of the den.

Setting.—The time for setting and making the arrangements for emptying is approximately fifteen minutes.

Excavating.—To excavate the block of superphosphate, the movable end wall G is raised out of the way, and the sides F allowed to swing clear of the material. The mechanical excavator H is then started up, and at the same time the movable carriage commences to traverse the excavator against the superphosphate. As the mechanical excavator advances, the parts of the den mounted on the same carriage recede from the block of superphosphate; thus the material is continually exposed to the cutting action of the excavator knives. These cutters cut the material away to within 1 inch of the concrete block forming the back of the den, and deliver it over the side into the conveyor.

The thin shavings cut from the block of superphosphate are further disintegrated in falling into the conveyor—there is an absence of rubbing or pressure, thereby giving an exceptionally fine product.

Fig. 40 shows a complete Sturtevant superphosphate plant with the den in position for charging.

The Sturtevant excavator revolves at a speed of approximately 11 revolutions per minute,

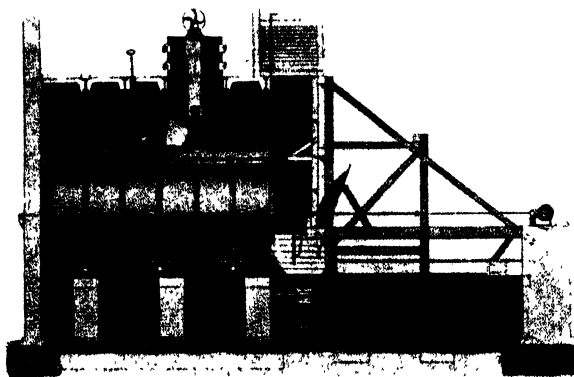


FIG. 38.—MILCH MECHANICAL DEN

which gives the cutting knives a speed of 600 feet per minute. This high cutting speed generates an air current which passes across the face of the block of superphosphate during the process of cutting. This air current helps to aerate the superphosphate and drive off some of the moisture.

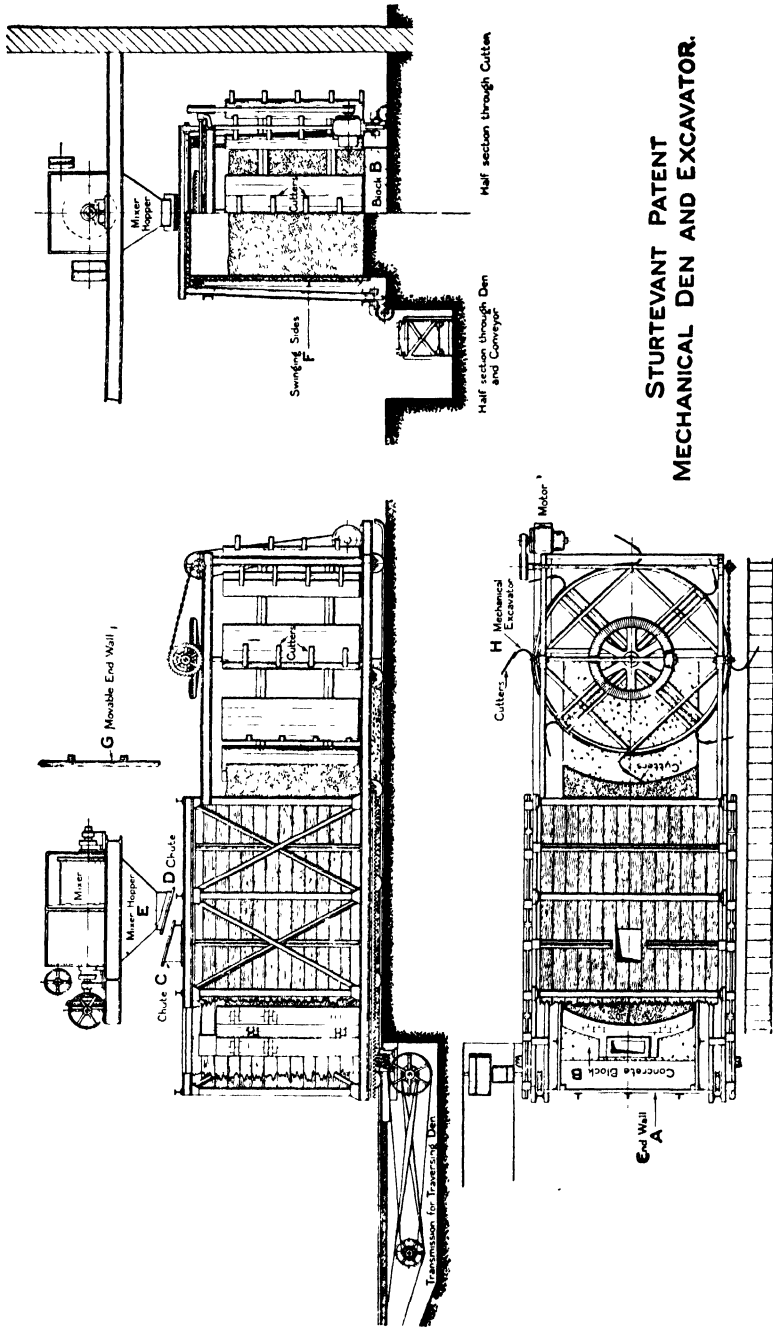
It is possible to obtain three charges from a 30-ton den in eight hours.

The time-table at one works is given as follows:

Mixing 50 batches—12 cwt. each	. . .	1 hr. 10 min.
Interval before cutting out	. . .	15 "
Time to cut out	. . .	37 "
Time to return den	. . .	5 "
Time to close up ready for mixing	. . .	23 "
		<hr/>
		2 hr. 30 min.

The power required to operate is 7 b.h.p. for the excavator and 3 b.h.p. for traversing the chassis.

Figs. 41 and 42 are photographs of superphosphate produced by mechanical dens of the batch type. The former shows the porosity, and the latter the granular product as it comes from the excavator—95 per cent passes a 6-mesh screen.



**STURTEVANT PATENT
MECHANICAL DEN AND EXCAVATOR.**

FIG. 39.—STURTEVANT MECHANICAL DEN

American Practice.—The developments in the fertiliser industry in the United States of America have generally been along lines somewhat different from those followed in the European field. The largest works confine themselves solely to the manufacture of superphosphate, and many of them are designed on a very large scale.

In Europe a fertiliser factory is considered large if it produces 60,000 tons of superphosphate per annum. In America there are works producing 300,000 tons and over in the same time. The Davison Chemical Company at Baltimore has a plant capable of producing 1500 tons of superphosphate per twenty-four hours.

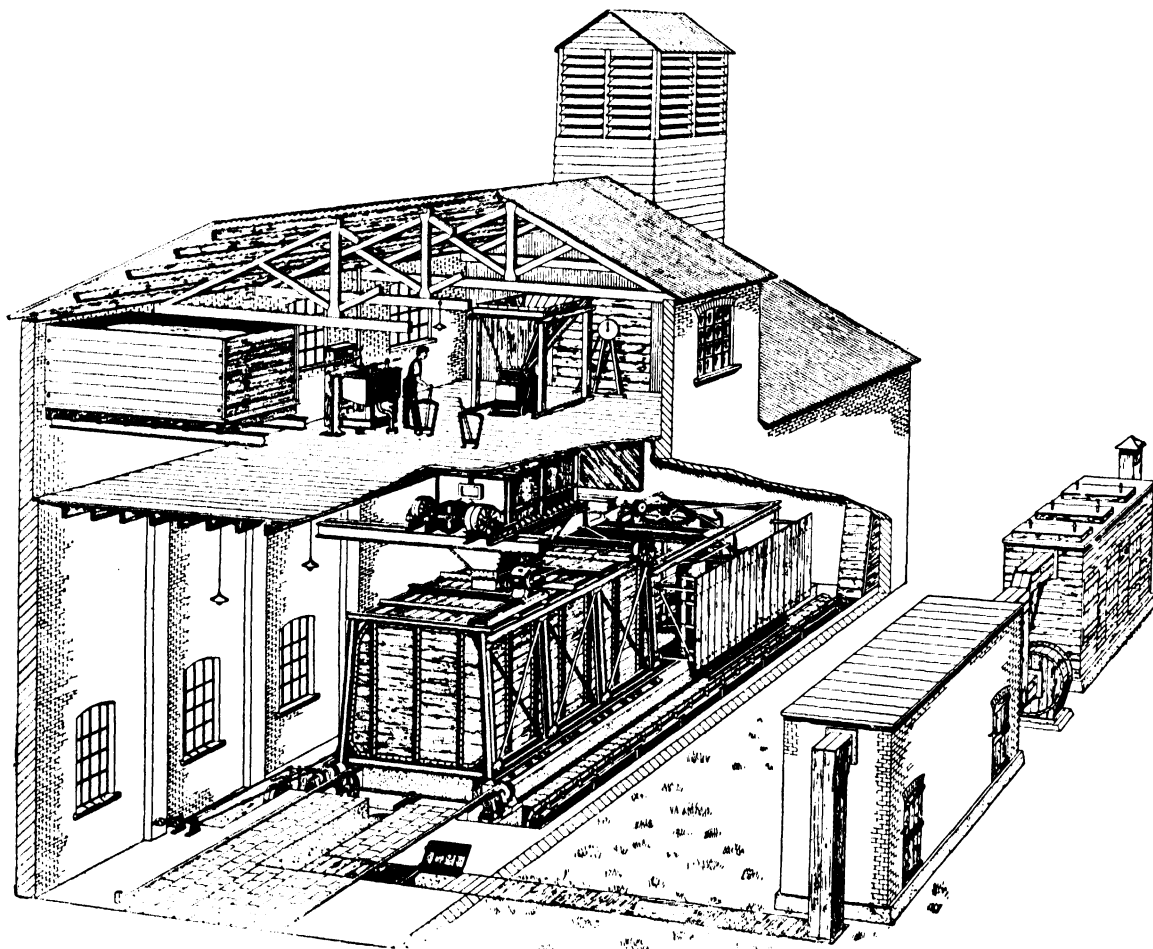


FIG. 40.—STURTEVANT SUPERPHOSPHATE PLANT

Mechanical dens, such as have been described, have not so far been adopted to any great extent in America, although European progress is keenly watched, and European methods are now being adopted in many instances at the smaller works.

The Svenska and Sturtevant mechanical dens are to be found in factories scattered throughout the country, but the crane-type excavator, exclusively used in the United States of America, undoubtedly holds the field at present.

Where this system is at work, the dens consist of large square chambers, built of concrete, standing approximately 40 feet high. They are usually about 15 to 20 feet square, and open at the top. Each holds approximately 150 to 250 tons. There may be two, four, or six in a line at the end of the superphosphate store, as shown in Fig. 33.

The store building is generally from 75 to 100 feet span, and approximately 500 feet long. An overhead crane traverses the whole length of the building, and acts as the excavator. Where there are two dens, one movable platform is mounted on top (see Fig. 33) and travels over the two

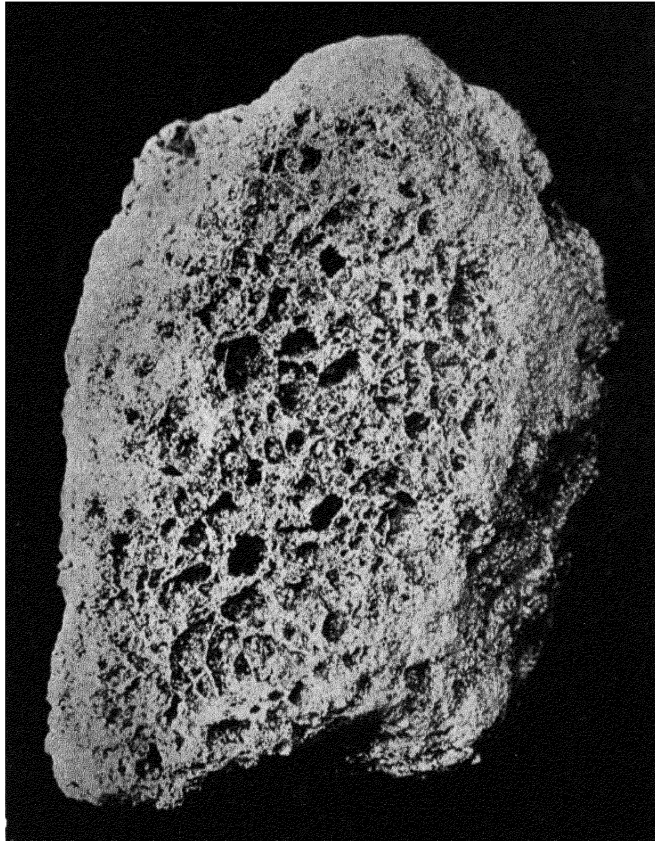


FIG. 41.—SUPERPHOSPHATE PRODUCED BY MECHANICAL DENS

dens, making its own seal with either of them. When there are four dens in a line, there are two movable platforms, each serving two dens.

On these movable platforms (see Fig. 33), previously referred to, are mounted two mixers of the vertical type, two acid-measuring tanks, and two phosphate weighers. Three men are usually

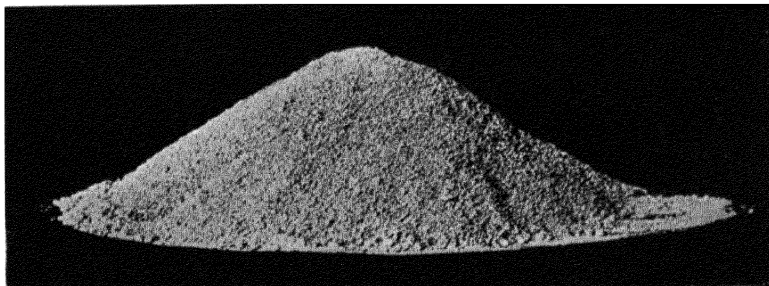


FIG. 42.—SUPERPHOSPHATE AS DUMPED ON THE PILL

employed to operate the mixing apparatus, and it takes approximately six hours to charge a den holding 250 tons. The superphosphate is generally allowed to remain in the den over-night. The

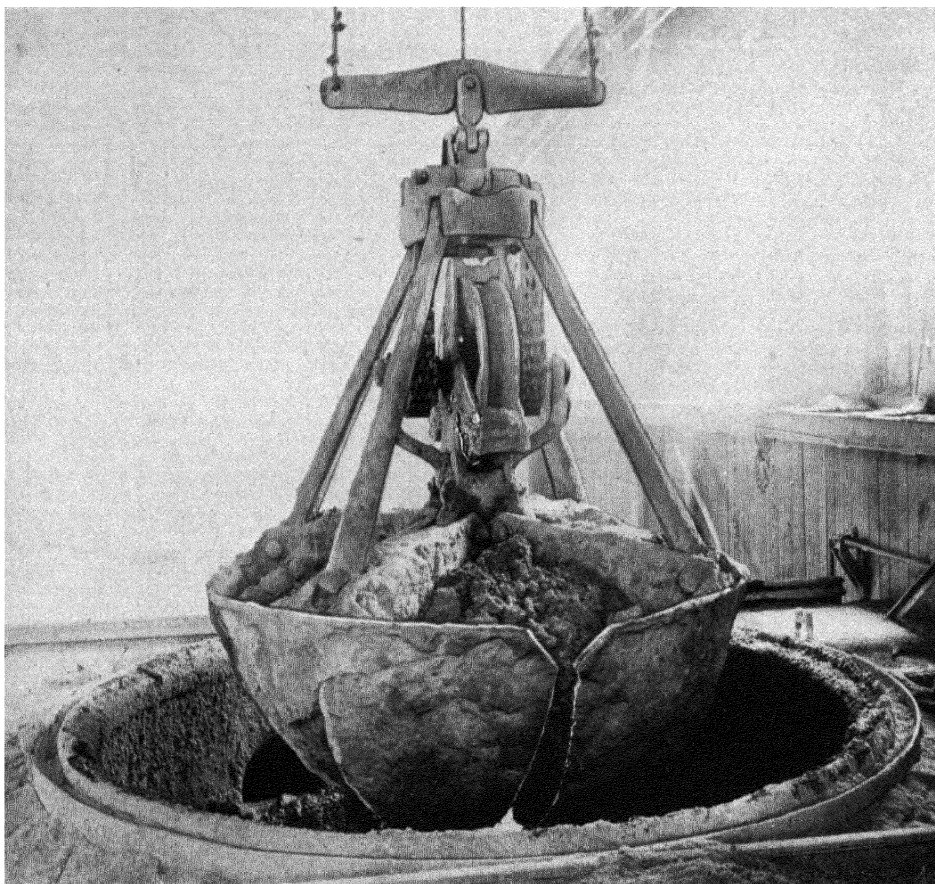


FIG. 43.—ORANGE PEEL BUCKET

excavation is accomplished by means of the overhead electric crane, which is fitted with a grab, or "orange-peel" bucket. The bucket is lowered into the den, picks up its load, and takes it direct to the storage heap. These buckets lift as much as 3 tons at a time, and will excavate 250 tons in approximately five hours, dependent upon how far the crane has to travel with its load.

Fig. 43 shows an "orange-peel" bucket emerging from a circular den with its load of superphosphate.

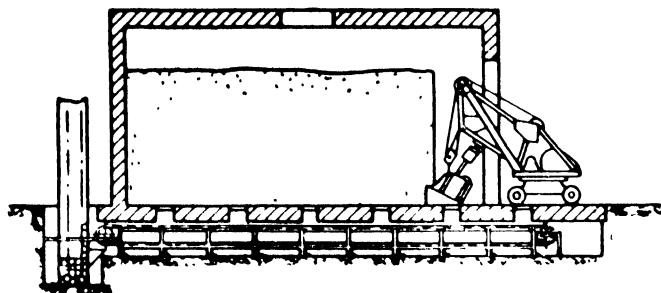


FIG. 44.—STATIONARY DEN WITH THEW SHOVEL EXCAVATOR

One den is being charged while the adjacent den is being excavated.

Superphosphate produced in this way is not in such good physical condition as that produced by fine-cutting mechanical dens. However, the system has proved its suitability where large outputs are aimed at, and it is doubtful whether it will ever be superseded.

“Thew” Shovel Excavators.—Another method of excavation employed in the United States of America is illustrated in Fig. 44. The den is rectangular in shape, and some are built to hold 600 tons. They are constructed of concrete, and have a movable door at one end, similar to the

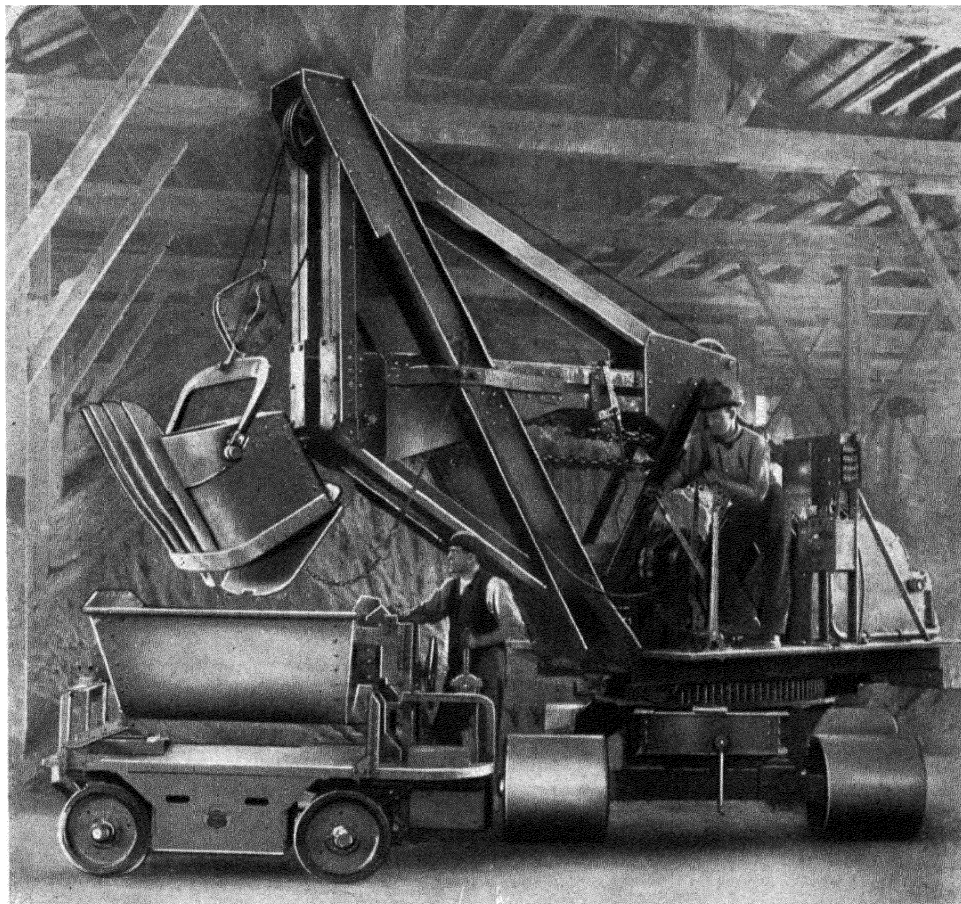


FIG. 45. THEW SHOVEL.

old-fashioned hand dens. Along the bottom of the den there is a series of openings with movable covers. These openings connect with a subway, in which is situated a tray conveyor.

The superphosphate is excavated by means of a Thew shovel, which travels into the den under its own power and digs into the face of the block, dropping the contents on to the floor. The superphosphate falls through the openings on to the tray conveyor, and thence to an elevator, which raises it to a height for distribution in the store.

Three men are generally required to operate this system. One man operates the excavating shovel and two men push the superphosphate down through the openings.

The wear and tear on the machine is heavy. It generally excavates at the rate of 50 to 60 tons per hour. Fig. 45 shows the Thew excavator, which may be driven either by steam or electricity.

✓ CHAPTER VII

MECHANICAL DENS AND EXCAVATORS—CONTINUOUS TYPES

CHEMICAL engineers seek, wherever possible, to translate their processes into continuously operating ones, as distinct from the intermittent type. There are obvious advantages, not the least of which is that continuous production ensures a minimum cost, from the point of view of capital expenditure.

But there are others, which are not less significant. Having established a set of conditions which is calculated to promote the highest efficiency, such conditions can best be maintained in a continuous plant, as distinct from an intermittent one.

Again, given uniformity of quality of raw materials, the standards with which one must comply, as regards quality of the final product, can best be maintained by continuous rather than by batch working. Moreover, power and other costs must be more favourable with continuous operation, because one avoids abnormal horse-power absorption, due to starting torques, which are inseparable from intermittent working.

Doubtless these and other considerations have led chemical engineers to seek to establish continuous processes for the manufacture of calcium superphosphate.

In this country two types of continuous dens have been adopted: one is the Broadfield, the other the Maxwell. The former results from the ingenuity and continued enterprise of American chemical engineers, and, strange to remark, it has been adopted to a greater extent in this country and on the Continent than in the United States. The other continuous den—the Maxwell—is the invention of Mr. A. Wilson, the manager of J. & W. Maxwell's works, Silloth, near Carlisle. This process has been in operation for ten years now, but it does not appear to have gained favour to any marked extent.

On the European continent one finds two continuous den processes, viz., the Moritz-Standaert and the Nordengren. The Moritz-Standaert has been installed at four works. The Nordengren has been erected as a large unit, and invokes confidence.

The Broadfield Process.—Being continuous in operation, the flow of acid and phosphate is controlled quite differently from that used in the batch system previously described. A flow sheet of the process is given in Fig. 46.

Acid is fed continuously to the mixer by a simple and efficient arrangement. The rate of flow is constant, and it is only necessary to make a simple adjustment to change the setting to suit different grades of phosphate rock.

The ground phosphate rock is also supplied continuously to the mixer, and to all practical purposes there is no fluctuation in the rate of feed.

An important point is that the Broadfield unit improved design feeder gives a uniform rate of feed, irrespective of condition of wear of mechanical parts.

The quantity of ground phosphate can be increased or decreased by varying the speed of operation.

The acid and phosphate thus measured feed continuously to the mixer.

The mixer consists of a cast-iron trough, U-shaped, placed horizontally and built in sections, so arranged that they form two compartments—one for mixing and one for kneading. The mixing compartment is slightly deeper and forms one section.

A square shaft revolves in the trough, on which are mounted a number of specially designed paddles clamped to the shaft and so arranged that they effect an alternate advancing and retarding action. These paddles, being made in two halves, can be quickly changed to suit different grades of phosphate.

The mixer is kept under a strong suction by means of a powerful fume exhaust fan, which withdraws as much as possible of the gas and steam evolved during the violent chemical reaction in the mixer.

The long duration of the mixing—4 to 5 minutes—together with the powerful suction employed, help considerably to effect a more intimate chemical reaction between the acid and phosphate and to reduce the moisture content in the resultant superphosphate. By the time the mixture of phosphate and acid has passed through the mixer it has become a thickened fluid and just mobile enough to level itself when falling into the conveyor den below.

The den consists of a moving endless conveyor with two similar conveyors forming side walls. In the early models these conveyors were formed with wood slats attached to pin type chain.

To-day steel slats are used for the floor of the den conveyor, which are more durable and reduce maintenance charges.

These three conveyors together form a closed compartment, and they move slowly forward and convey the mass of superphosphate towards a set of revolving knives or cutters. These shave off the superphosphate in a coarse or finely-divided state, according to the speed of rotation of the revolving knives, and the superphosphate then falls to a belt conveyor which conveys the material to the store.

The length of time the superphosphate remains in the moving den is about 70 minutes. Owing to improved mixing and kneading in the mixer this time is much less than in the earlier installations.

Broadfield plants are designed for a capacity of 5–6 tons, 10–12 tons, and 20–25 tons per hour, the intermediate size of plant suiting best the average works in this country.

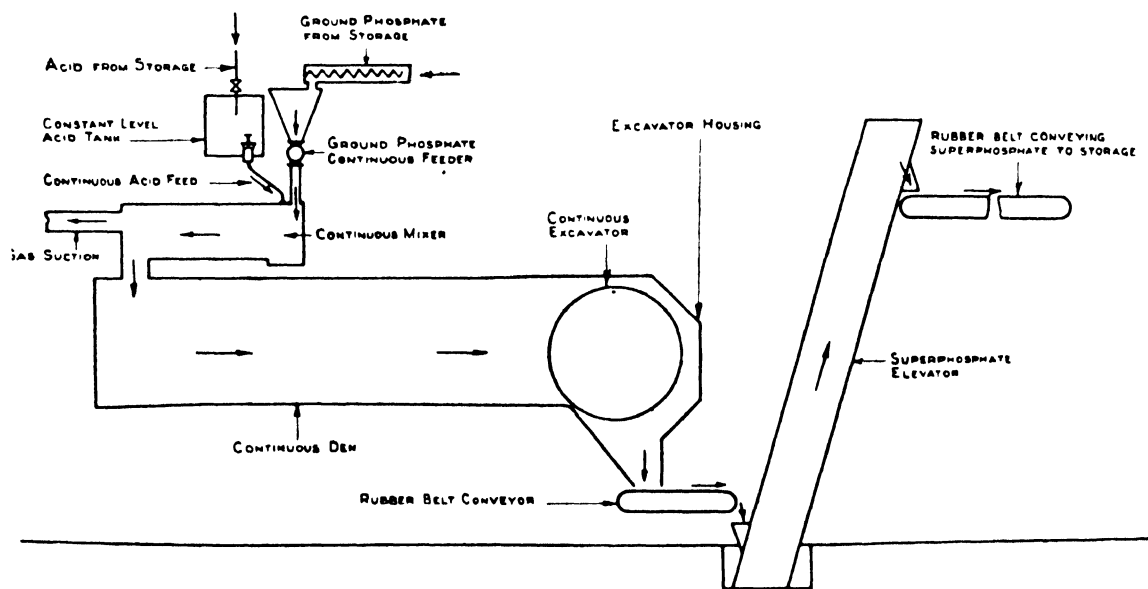


FIG. 46.—FLOW SHEET OF THE BROADFIELD PROCESS

Fig. 47 shows the arrangement of a plant having a capacity of 20–25 tons per hour. This size at some works is producing 27 and as much as 30 tons of superphosphate per hour.

To date, twenty-five Broadfield plants of varying capacities have been installed in Europe, U.S.A., South Africa, Egypt, Australia, and New Zealand.

Stronger acid is used than with batch type dens, the usual strength being 127° Tw. The phosphate is ground to varying finenesses from 70 to 90 per cent through 100-mesh British Standard sieve, according to the grade and physical qualities of phosphate used and reaction required.

The following are typical analyses of superphosphate made by the Broadfield process.

TABLE 22

Phosphates.	Gafsa 63.5%	Constantine 63.4%	Morocco 73.6%	Morocco 69.7%	Kosseir 65.2%
Days after mixing	90	90	34	3	58
Water-soluble P_2O_5	16.65	17.10	19.39	18.14	17.60
$Ca_3P_2O_8$	36.38	37.37	42.37	39.64	38.46
Insoluble P_2O_5	0.77	0.58	0.84	0.85	0.54
$=Ca_3P_2O_8$	1.68	1.27	1.84	1.86	1.18
Moisture	10.57	9.92	8.55	9.65	9.41
Free acid (P_2O_5)	1.35	2.70	1.20	2.52	2.95

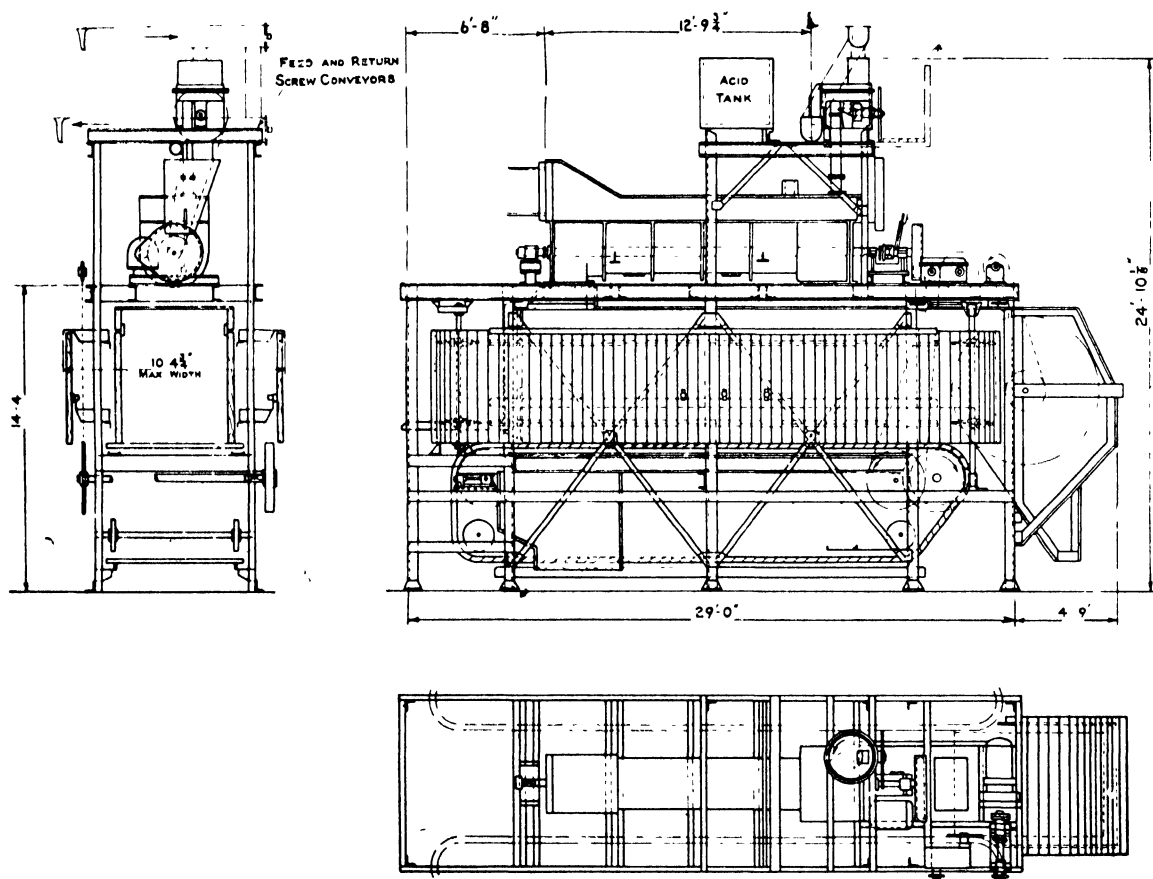


FIG. 47.—ARRANGEMENT OF BROADFIELD ACIDULATING PLANT

The Maxwell Process.—A Maxwell continuous den is shown in Fig. 48, and the shape of this den may be likened to a very much enlarged motor-car tyre in an upright position. The trough, forming this so-called tyre, is made of cast steel, and in a 5 tons per hour den is about 19 feet in external diameter and approximately 5 feet 6 inches cross sectional diameter. It is built up of

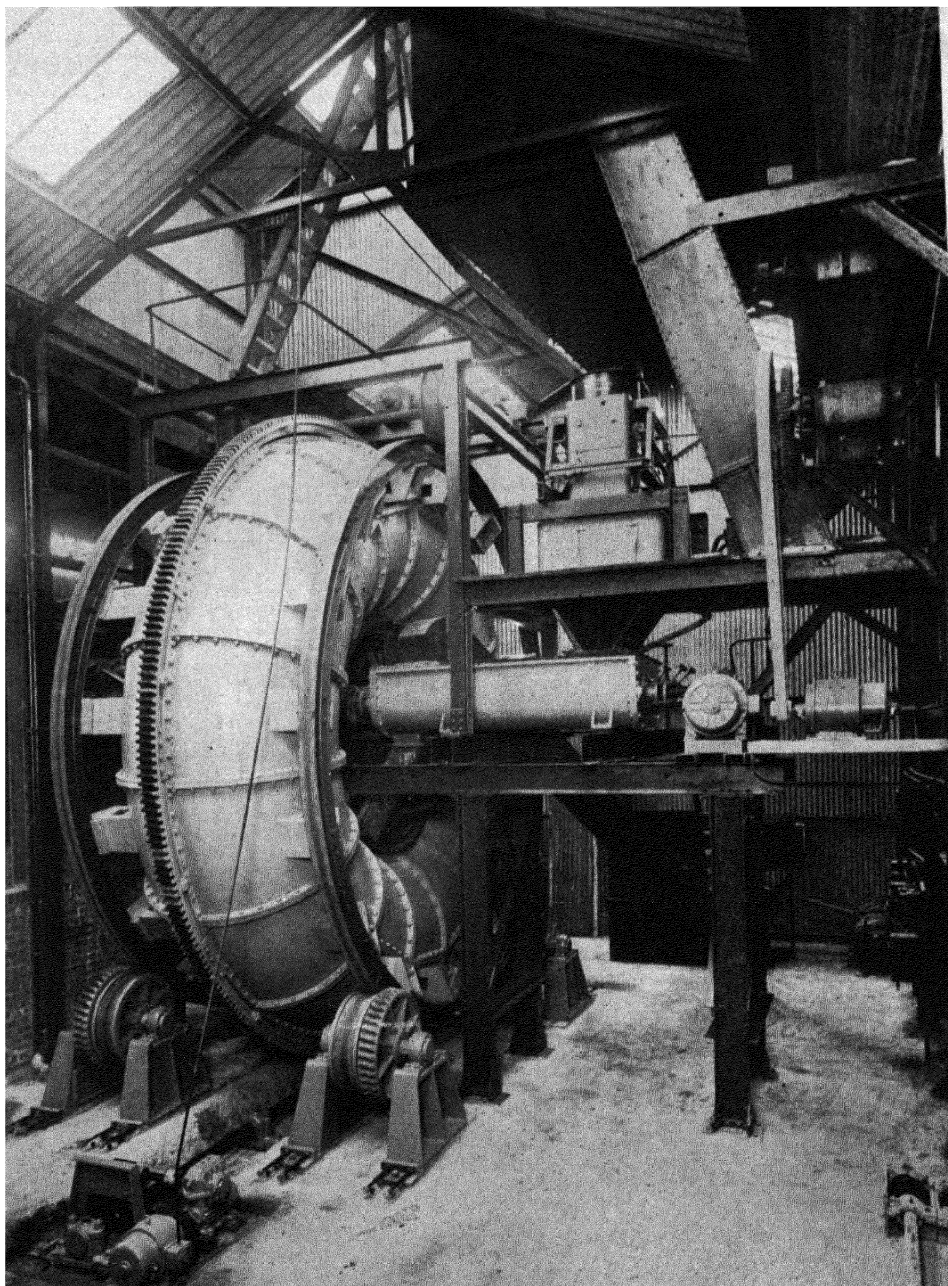


FIG. 48.—MAXWELL CONTINUOUS DEN

sections having flanged joints accurately machined. The den is supported on two roller tracks formed of rolled steel joists, which in turn rest on four rollers firmly secured to the floor. A large gear ring is mounted on the circumference of the den on the centre line, and by this the den is rotated. A forged steel worm engages with the large gear ring at the ground level. Further worm reduction gear is employed between this shaft and the motor driving the den, as the total reduction is approximately 170,000 to 1, the den only making one revolution in four hours. The power required to drive the trough is only about $1\frac{1}{2}$ h.p. The den shown in the illustration Fig. 48 has

The upper part of the container forming the den is closed by means of a concrete floor, which supports both a stationary partition, suspended within the container, and a mechanical cutter, which is driven through suitable reduction gear, mounted on the den top. On this floor one finds the superphosphate mixer, the volumetric phosphate feeder and the rotary acid feed (see Fig. 49).

The annular opening at the bottom of the rotating container is closed by stationary cast-iron sealing plates, which ensure a tight joint between the stationary and rotating parts, and also ensure cleanliness in operation. The superphosphate discharged from the mixer fills the annular space in the container formed between the concrete wall and the cast-iron central mandrel. This newly made superphosphate is prevented from spreading back to the cutter by the curved partition

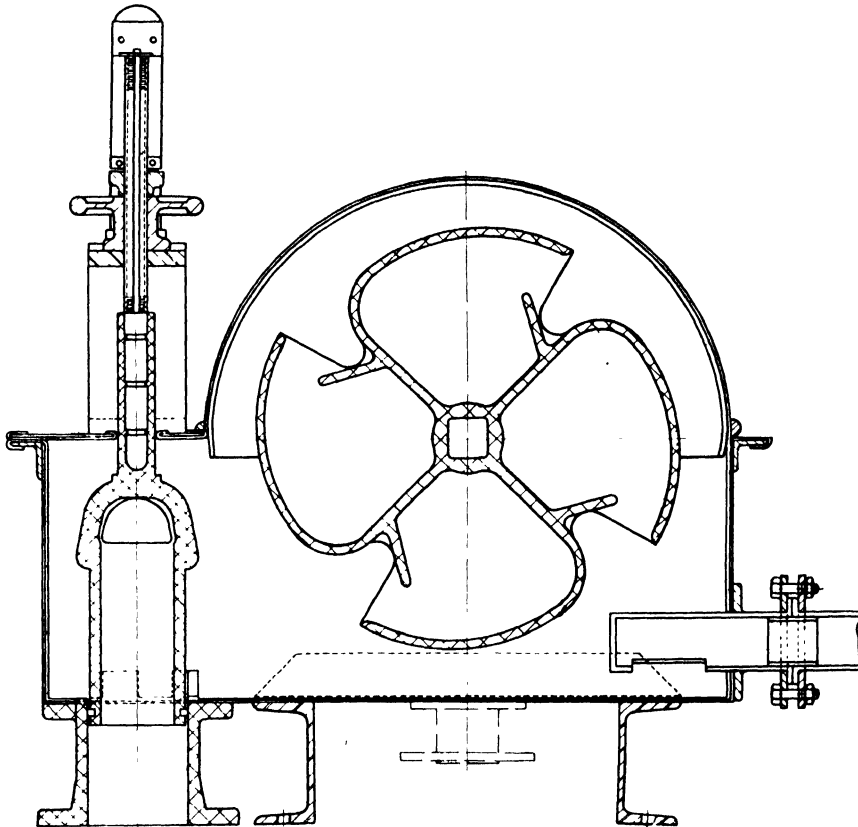


FIG. 49.—ROTARY ACID FEEDER

supported from the den top. The superphosphate hardens during the slow rotation of the den and forms a ring which regularly comes in contact with the revolving cutter, and is shaved off in fine even particles.

From the den the superphosphate falls on to a belt or steel tray conveyor, and is conveyed to storage.

During the process of mixing and cutting out a powerful suction fan draws away the fume and steam liberated by the chemical action, and a reasonably dry superphosphate is the result. The moisture is approximately 12 per cent as the product falls from the den.

The container makes one revolution in 2 to 4 hours, according to the capacity of the den, and the quality of raw phosphate used.

a capacity of 5 tons of superphosphate per hour. The trough weighs approximately 22 tons empty and 34 tons when full, and at one revolution in four hours gives two hours setting time. This may be varied according to the phosphate used. The inner circumference of the steel trough is made open, but a seal is made with a stationary wooden covering having openings at different points for (a) the slurry from the mixer, (b) the exit of the toxic gases, and (c) the discharge of the superphosphate as it is cut by the slicing device.

The den operates as follows: the slurry from the mixer is fed into the trough on the inner circumference somewhere near bottom dead centre. Superphosphate sets rapidly, and the mass while being carried upward holds together and does not slide back, as might be expected. At top dead centre the solidified superphosphate meets a revolving cutter mounted in the axis of the trough at right-angles to the direction of rotation. The cutter shaves off the superphosphate in a manner similar to most other types of dens and it falls into a chute and may be delivered by a conveyor to the store. There is one feature of the Maxwell den which others do not possess, and that is the superphosphate is delivered at a fairly high level which obviates conveyors or elevators having to go below ground level. At a point near the cutter on the inner circumference is attached the fume exhaust duct. A fan is connected to the duct and maintains a slight vacuum in the trough. The cutter in the Maxwell den requires 5 h.p. for driving.

Mr. Sven Nordengren, of Landskrona, has developed a large continuous superphosphate process (50 tons per hour), of which details are given in Fig. 48a. With this process less power and greater regularity of operation are claimed than with any other process. It is understood that the size of the Landskrona unit, carrying on the conveyor, as it does, 150 tons, is three times that of any other unit. For time factors (mixing, solidifying and in the chamber) see page 75.

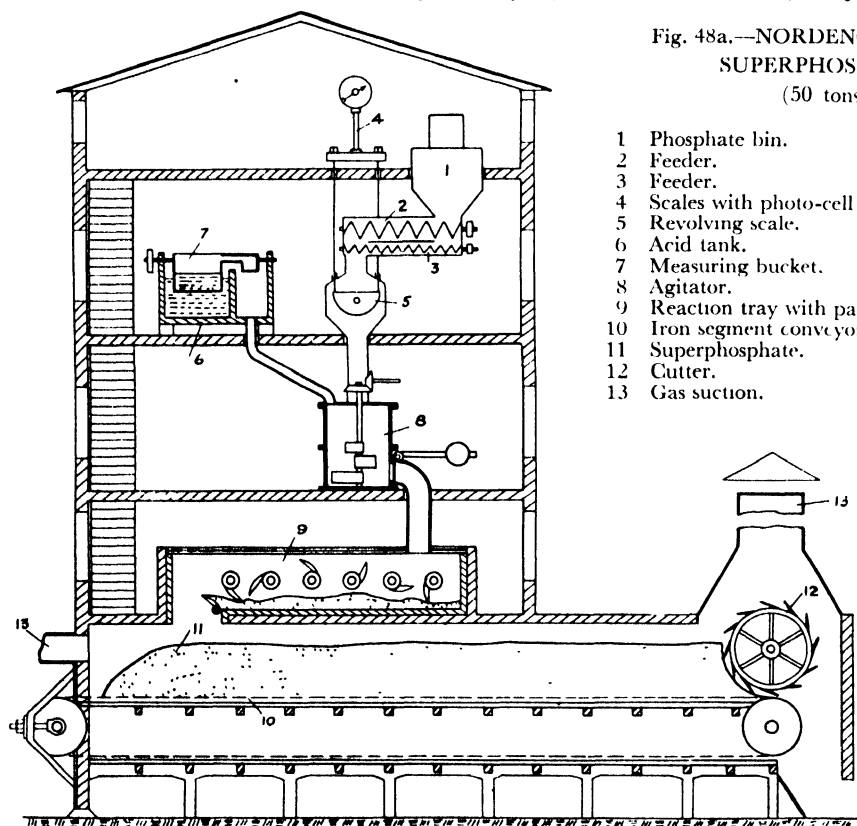


Fig. 48a.—NORDENGREN CONTINUOUS SUPERPHOSPHATE PROCESS

(50 tons per hour)

- 1 Phosphate bin.
- 2 Feeder.
- 3 Feeder.
- 4 Scales with photo-cell arrangement.
- 5 Revolving scale.
- 6 Acid tank.
- 7 Measuring bucket.
- 8 Agitator.
- 9 Reaction tray with paddles.
- 10 Iron segment conveyor.
- 11 Superphosphate.
- 12 Cutter.
- 13 Gas suction.

The Moritz-Standaert System.—There are now a number of these dens working in England, having capacities varying from 7 to 20 tons per hour. The Moritz-Standaert superphosphate den comprises a concrete cylindrical container, with a cast-iron central mandrel. The container rotates slowly at a variable speed on supporting rollers, and is driven through a toothed worm wheel and worm: it is kept centred by means of the supporting rollers.

Fig. 50 shows sectional views of the Moritz-Standaert den, and with the above description the process can be followed.

The power absorbed is comparatively small.

For a 10-tons per hour capacity den the total power is 1.7 kW.h. per ton of superphosphate made. This includes all the equipment up to the arrival of the product on the conveying band.

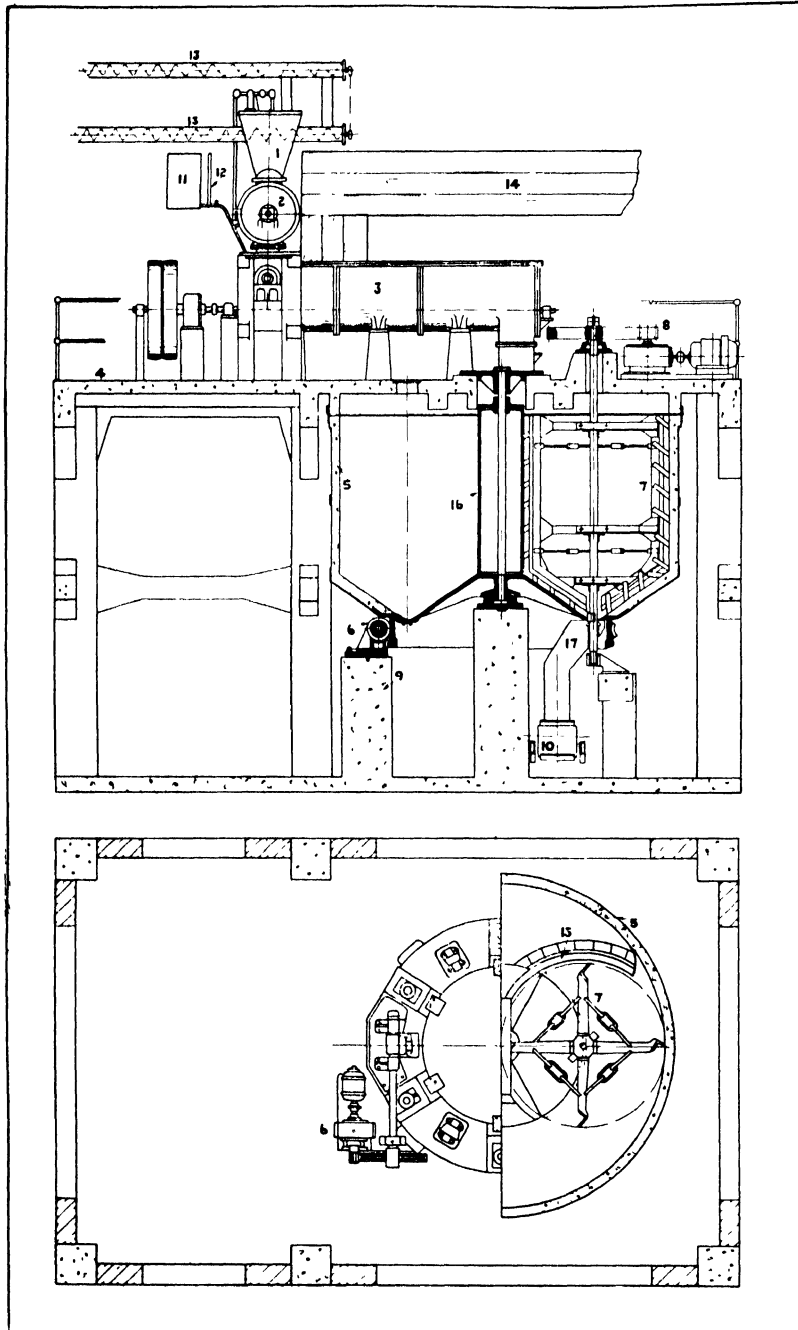


FIG. 50.—SECTIONAL VIEWS OF THE MORITZ-STANDAERT DEN

For a 20-tons per hour den, the total power is 1.0 kW.h. per ton of superphosphate made.

In all the continuous processes described the feeders for both the ground phosphate and the acid are volumetric in design. It is probably in these devices that improvements can still be made. Ground phosphate rock is not an easy material to control volumetrically.

In the Moritz-Standaert process one man supervises the plant, irrespective of capacity. The arrangement of the mechanical parts on the upper floor permits centralisation of the controls. Should the motor driving the cutter accidentally "cut out" it is interlocked with the motor driving the den traverse, so that it also comes to a standstill, and prevents serious trouble.

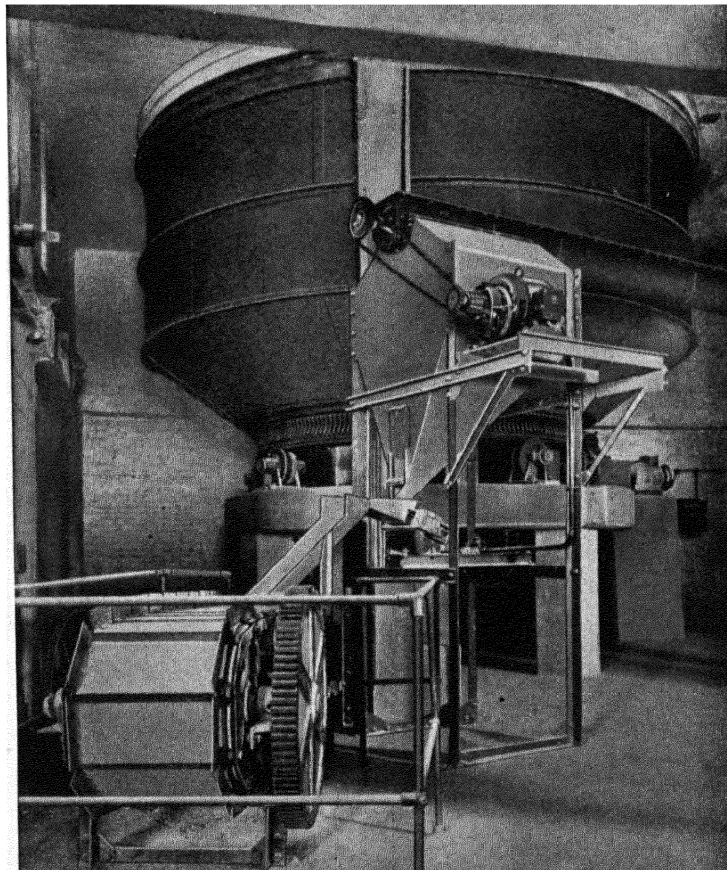


Fig. 51.—A MORITZ-STANDAERT CONTINUOUS DEN SHOWING CONVEYOR WHICH TAKES DELIVERY OF THE SUPERPHOSPHATE FROM THE DEN.

The following are the analyses of superphosphate made in the Moritz-Standaert den when using Morocco and Florida "hard rock" phosphates, the analysis being made six days after production.

	Morocco.	Florida.
	Per cent.	Per cent.
Water content	10.3	10.55
Total P_2O_5	18.8	19.39
Soluble P_2O_5	18.3	18.84
Free phosphoric anhydride	3.8	5.91
Citrate soluble P_2O_5	—	19.33

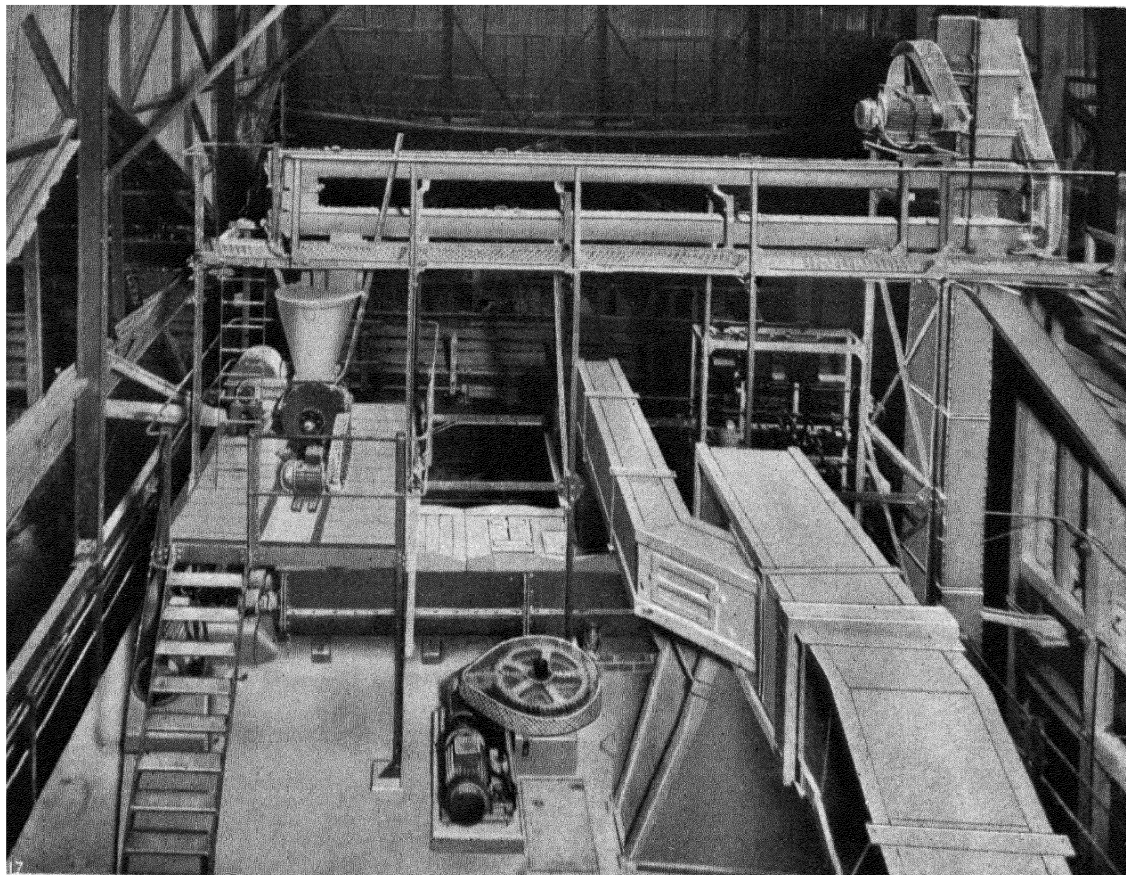


Fig. 52.--VIEW LOOKING ON TOP OF A MORITZ-STANDAERT CONTINUOUS DEN SHOWING MIXER AND PHOSPHATE AND ACID FEEDERS

The introduction of the continuous den was not altogether a revolutionary step in the manufacture of calcium superphosphate. In the opinion of many technicians it is still an open question whether the resultant product is superior to that manufactured by the batch process, or whether the cost of production has been reduced. That the continuous den possesses an advantage as regards transportation of the product to the store is conceded: continuity of operation is clearly to be preferred to intermittent discharge of the product.

The authors have had opportunities of studying the operation of the various continuous processes, and noting what is possible with each of these methods

In the Broadfield and Moritz-Standaert systems special attention has been given to the mixer. The time factor can be varied and is increased over other types. An adequate draught is provided on the mixer to remove as much of the steam as possible, and so cut down the percentage of moisture. The fan on these dens provides a draught equivalent to approximately 1300 cubic metres of air per hour at 110° F. for every ton of superphosphate produced in the same period.

In fact the superphosphate is kept as long in the mixer as possible without endangering its discharge.

Both dens, by means of their construction, conserve the heat of reaction and complete the process of acidulation.

From the viewpoint of cleanliness the Moritz-Standaert is a distinct advance on all the other systems, and is indeed unique.

Figs. 51 and 52 are illustrations of Moritz-Standaert dens working in Great Britain.

✓ CHAPTER VIII
THE OBERPHOS PROCESS

AS previously mentioned, this process was operated for a time by Messrs. Fisons, Ltd. The process is unique, in that it is intermittent in operation, and involves the use of an autoclave, and hence the temperature and pressure of reaction are dissimilar to those of the normal processes. It produces a dry gritty granular superphosphate, sensibly different in appearance from the porous material made by other processes.

The Oberphos process is a definite departure from all others, and was evolved at the works of Ober & Sons, Baltimore, U.S.A.

The acid used is of the same strength as in the batch process, viz. 115° to 120° Tw., but the temperature of the acid entering the autoclave ranges from 90° to 120° F. In this process there is no actual mixer in which the phosphate and acid are mixed and kneaded before solidifying. Both the phosphate and acid are weighed because the system is a batch one.

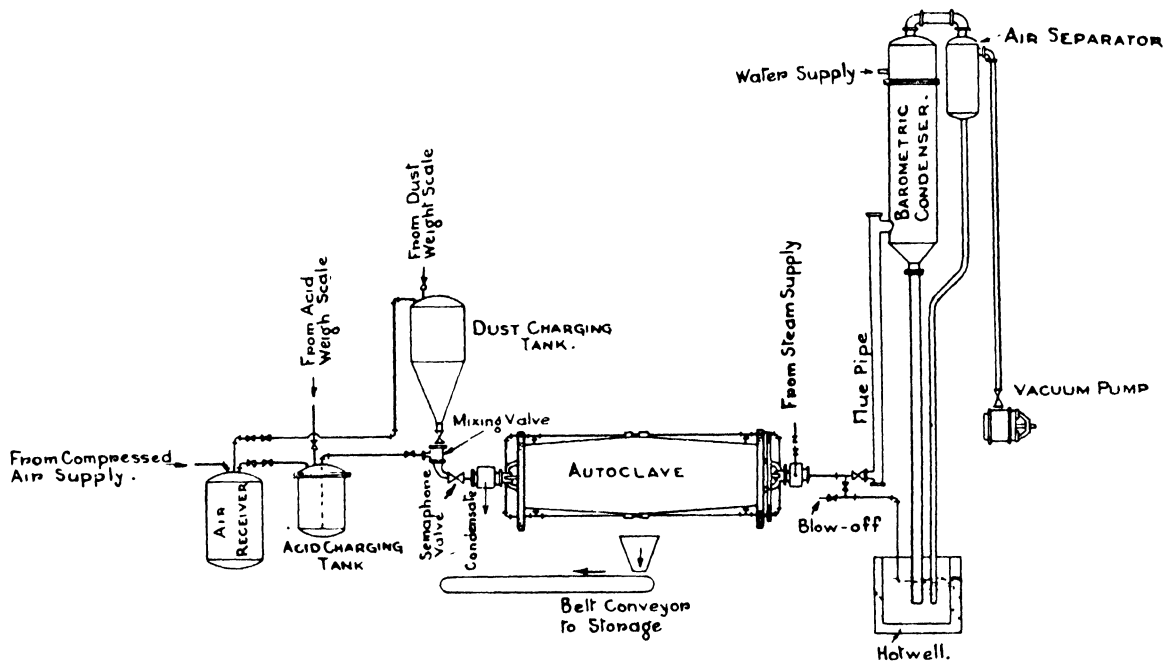


FIG. 53.—FLOW SHEET OF OBERPHOS SYSTEM

If North African phosphate is used, it is ground to a fineness of 80 per cent through 100-mesh British Standard Sieve. In the case of Morocco or Florida phosphate the fineness is greater, being 85 per cent through 100 mesh. The principle of the process is as follows and reference should be made to the diagram, Fig. 53.

Ground phosphate rock and sulphuric acid are rapidly charged into a revolving drum termed an autoclave. The drum is sealed off immediately after charging and direct steam is introduced to the extent of about 30 to 50 lb. of steam per ton of material. Gradually CO₂, hydrogen fluoride and perhaps some hydrochloric acid, are evolved, in the presence of the steam which is introduced in the ordinary course. The pressure obviously accumulates, until a predetermined one is reached. But before this, the evolution of the normal decomposition products will be arrested.

The said pressure coincides with a specific temperature, which is said to be of the order of 150°C . The pressure period lasts for thirty to forty minutes, when the products of decomposition and steam are exhausted. This can be effected in such a way that having regard to the sensible heat of the superphosphate mass, the moisture content is of the order of 11 per cent, which relates to a temperature of about 50°C . When this temperature is reached, the rotation of the autoclave is arrested, the manhole cover removed, and the autoclave is again revolved, in order to discharge its contents. Superphosphate is deposited into a hopper, from which it is conveyed to the store by

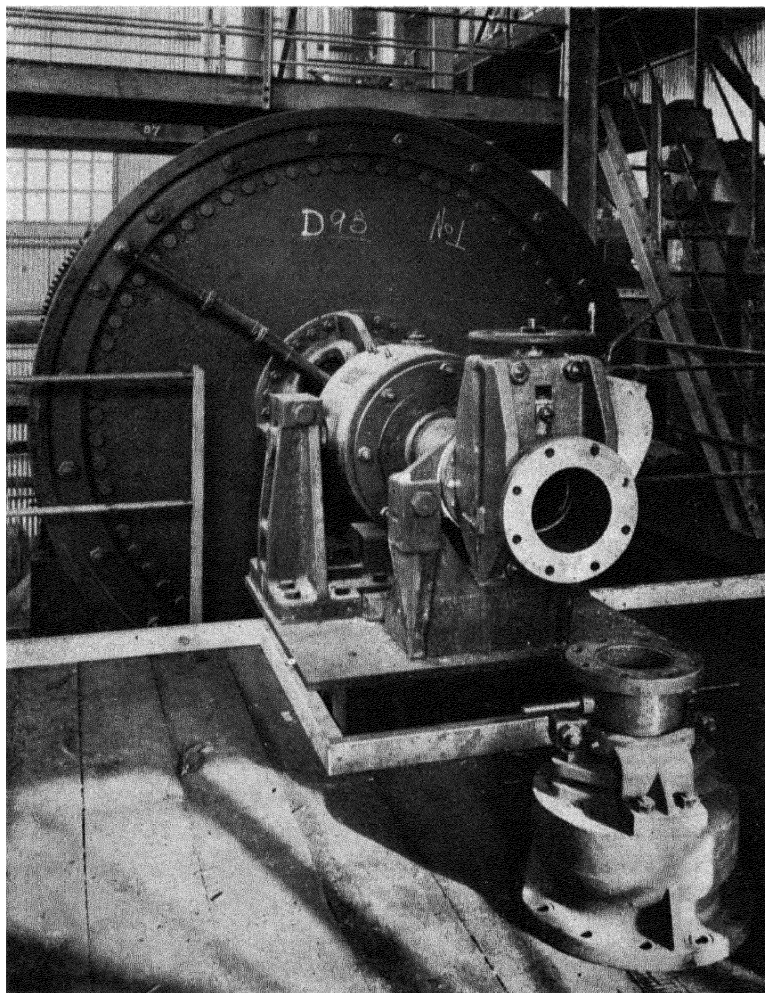


FIG. 54.—MIXING VALVE IN OBERPHOS SYSTEM

means of an india-rubber belt. It should be noted that the autoclave is a jacketed one, in which steam is used, acting as an insulating medium apart from aiding the maintenance of a predetermined temperature.

The batch charge is approximately 8 tons in all, and the introduction of phosphate and acid takes about 90 seconds. The speed of the autoclave is 5 revs. per min. It consists of a welded steel shell lined with lead which is autogenously welded to the steel shell.

The mixing valve at the feed end of the autoclave is an ingenious device, and is shown in Fig. 54.

The acid enters the valve tangentially at an extremely high velocity and the ground phosphate is introduced through the centre. In this manner an extremely efficient pre-mixing of the acid and rock is obtained before entry to the vessel.

By means of recording instruments, it is possible to compare the way in which each kind of phosphate affects conditions inside the autoclave.

The greatest pressure is created by the lower-grade phosphates, because there is a greater quantity of CO_2 evolved. Care has to be taken that too much frothing does not block the vacuum line when the blow-off valve is released.

The complete cycle takes approximately 90 minutes and at the end of this time the superphosphate is in the form of hard round lumps containing approximately 11 per cent moisture. In texture it is quite different from the superphosphate made by other processes, although as far as

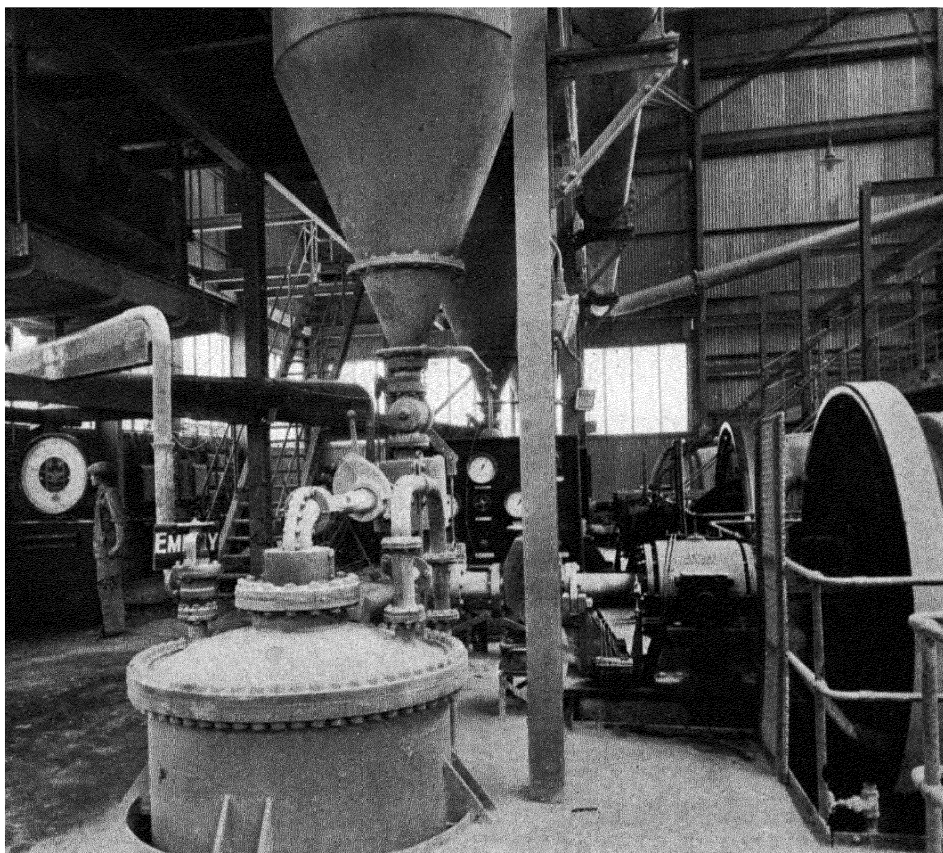


FIG. 55.—GENERAL VIEW OF OBERPHOS PLANT

it is yet known, the chemical composition is almost similar. Owing to its texture, it can be ground almost to any degree of fineness; the machine used for the purpose is described and illustrated on page 124.

The vacuum and condensing systems need only brief mention. The condenser is of the direct contact barometric type, and is equipped with the usual baffle plates over which the condensing water cascades. The vacuum pump is a reciprocating double-acting piston pump. The quantity of water used in the condenser is relatively large for the purpose of protecting the vacuum pump and is in the region of 300–500 gallons per minute. A general view of the plant is shown in Fig. 55.

TABLE 23

Phosphate.	Per cent. Acid actual.	Strength of acid ° B.	Temp. of acid ° F.	Size of batch lb.	Diges- tion time mins.	Vacuum time mins.	Age of sample hrs.	Soluble P ₂ O ₅ .	Total P ₂ O ₅ .	Mos- ture.	Free acid.	Analysis of rock.
Florida	.	53.8	80°	14,000	35	35	72	17.35	18.95	8.58	4.48	Ca ₃ P ₂ O ₈
"	.	53.8	100°	14,000	35	35	72	17.36	18.90	8.61	4.24	CaCO ₃
"	.	53.8	100°	14,000	35	35	96	17.48	18.93	8.77	4.00	H ₂ O
"	.	53.8	100°	16,000	35	35	72	17.37	18.87	9.84	3.78	Fe ₂ O ₃ .Al ₂ O ₃
"	.	53.8	100°	16,000	35	35	48	17.44	18.77	9.56	4.68	(
M'dilla	.	90.5	100°	16,000	20	35	72	16.09	17.53	10.64	2.84	Ca ₃ P ₂ O ₈
"	.	90.5	100°	16,000	20	35	48	16.08	17.38	11.00	2.92	CaCO ₃
"	.	90.5	100°	16,000	20	35	48	16.28	17.39	10.70	3.53	H ₂ O
"	.	90.5	100°	16,000	20	35	48	16.20	17.48	9.91	3.09	(Fe ₂ O ₃ .Al ₂ O ₃
Gafsa	.	92.8	120°	16,000	20	35	72	16.01	17.22	10.40	3.28	Ca ₃ P ₂ O ₈
"	.	91.7	120°	16,000	20	35	48	15.82	17.22	10.50	2.89	CaCO ₃
"	.	90.5	110°	16,000	20	35	48	15.71	17.18	10.44	2.82	H ₂ O
"	.	89.4	110°	16,000	20	35	48	15.74	17.56	9.78	2.37	(Fe ₂ O ₃ .Al ₂ O ₃
Morocco	.	90.5	120°	16,000	20	35	24	17.38	19.32	8.39	2.67	Ca ₃ P ₂ O ₈
67%	.	90.5	120°	16,000	20	35	48	17.42	18.86	9.02	2.06	CaCO ₃
"	.	90.5	120°	16,000	20	35	48	17.44	18.73	9.28	2.49	(H ₂ O
												(Fe ₂ O ₃ .Al ₂ O ₃
Morocco	.	92.9	120°	16,000	20	35	24	18.09	19.87	8.12	3.70	Ca ₃ P ₂ O ₈
74%	.	92.9	120°	16,000	20	35	96	19.14	20.52	7.88	2.70	CaCO ₃
"	.	92.9	120°	16,000	20	35	72	18.47	20.04	7.46	3.34	H ₂ O
"	.	92.9	120°	16,000	20	35	48	18.96	20.84	7.20	3.16	(Fe ₂ O ₃ .Al ₂ O ₃

Needless to point out, the Oberphos process involves the use of expensive plant, the autoclave alone weighs over 40 tons, and the control valves are made of acid-resisting steel. It is sold under licence and the patentees are paid a royalty on every ton of superphosphate made. It is exclusively used in this country by Messrs. Fisons, Ltd., and their associated company, National Fertilisers, Ltd.

Table 23 gives typical analyses of Oberphos superphosphate.

Microphotograph, Fig. 56, shows a nodule of superphosphate arising from a Sturtevant den. It reveals the irregular porous structure which one would associate with the irregular evolution of carbon dioxide and steam. On the other hand, microphotograph, Fig. 57, of a nodule of Oberphos superphosphate, shows a more regular structure. This is to be expected, having regard to the specific features of the Oberphos process. The material in the autoclave is no longer plastic (if, indeed, this condition is ever attained), when carbon dioxide and steam are evolved. The evolution of the latter gases is effected under conditions different from the ordinary den superphosphate process.

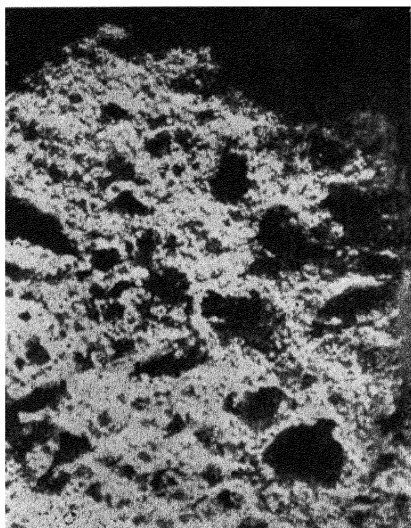


FIG. 56.—MICROPHOTOGRAPH OF A NODULE OF SUPERPHOSPHATE FROM A STURTEVANT DEN

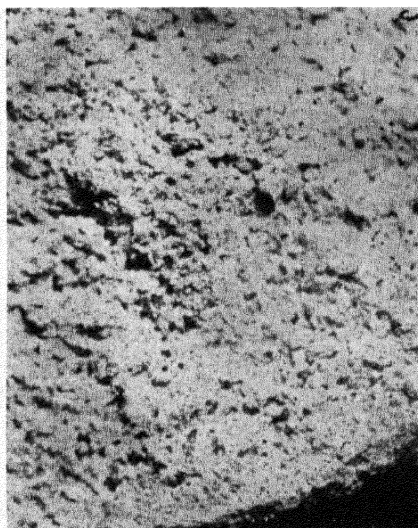


FIG. 57.—MICROPHOTOGRAPH OF A NODULE OF SUPERPHOSPHATE MADE BY THE OBERPHOS PROCESS

In point of fact, it is known that only about 20 per cent of the fluorides are decomposed, and this is to be expected, in view of the fact that while there is forced acid penetration through the rock phosphate, in the initial stages of the autoclavic process, there cannot exist the best conditions for the evolution of the gases, by reason of the pressure obtaining. Is not calcium silicofluoride formed within the mass of superphosphate made by this process, by virtue of the conditions prevailing?

Some particulars of the superphosphate factory at Avonmouth might, with advantage, be afforded here. Messrs. Fisons, Ltd., and Messrs. Imperial Smelting Corporation, Ltd., have combined their fertiliser interests in the West of England in National Fertilisers, Ltd., and have erected the aforementioned factory.

The area of the site covered by the complete plant is 12 acres: one hundred and ten contractors were employed in the construction of the factory, which is designed for an annual production of 75,000 tons of calcium superphosphate. An aerial ropeway, over two miles long, enables cargoes of raw material to be discharged at the docks and transported to the factory at the rate of 1500 tons per 8-hour shift. Similarly, the finished fertilisers can be loaded to ship in bulk for despatch to all parts of the world. The phosphate store is 300 feet long by 114 feet span, and has a capacity of

CHAPTER IX

ARTIFICIAL DRYING OF SUPERPHOSPHATE

IT should be remarked that the water content of superphosphate concerns, in the first place, water of the liquid phase, a solution of phosphoric acid, monocalcium phosphate, and secondary constituents: secondly, water of crystallisation of the salts. Equilibrium exists between these different phases, a knowledge of which is essential to an exact appreciation of how to estimate the water in the different states. The methods hitherto adopted for the determination of the water content of superphosphate have been open to objection, because they did not admit of the attainment of a sufficient measure of exactitude.

The estimation of the total water by drying in a drying oven at 100°C . leaves several loopholes for error to arise, some leading to a high result because of the loss of volatile fluorine compounds, some to a low result because certain hydrated salts do not lose their water at 100°C . Moreover, under the action of heat, and even merely of concentration, the internal equilibrium of superphosphate is profoundly modified.

Investigations have been conducted¹ to determine the minimum temperature of dehydration of the principal salts constituting superphosphate. A. Sanfourche and his associates have pointed out the following:

1. Gypsum at a temperature of 100°C . passes into the state of semi-hydrate: this at 120°C . loses almost all its water, retaining only 0.5 per cent of it, which only disappears very slowly.

2. Crystallised monocalcium phosphate— $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ —is stable at 100°C .: it becomes anhydrous at 120°C .: at 150°C . it commences to be transformed very slowly into pyrophosphate— $\text{CaH}_2\text{P}_2\text{O}_7$, which in its turn decomposes above 180°C .

3. Crystallised dicalcium phosphate— $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ —gradually loses its water of crystallisation at 100°C .: a singular fact, it loses at 120 – 150°C . more slowly than at 100°C .

4. Phosphates of iron and of aluminium retain at 120°C . a little more than their constitutional water, if one may use this term in regard to bodies which, in superphosphate, are not generally in the form of definite compounds. As, however, their proportion is small, the error to which this might lead is absolutely negligible.

5. The organic matter always present in superphosphate is not decomposed around 120°C ., any more than are the fluorosilicates in surroundings in which the acidity has been neutralised.

For many years superphosphate manufacturers appeared to be averse from drying superphosphate, because they suspected, rightly or wrongly, that reversion would occur. Sorel and Schucht have advanced many theories about reversion, but these have possessed an element of obscurity, and it has hardly been possible to disentangle a single leading idea from such commentaries. This particularly applies to what has been asserted by Sorel.

On the subject of reversion, it is necessary firstly to discriminate between the reduction—the lowering of the content of water-soluble phosphate—and the reversion—the lowering of the content of assimilable phosphate. By the latter is meant phosphate soluble in water and in citrate. Reversion is much less frequent than reduction, the gravity of which is only appreciated in countries where sales are based upon the content of water-soluble P_2O_5 .

¹ A. Sanfourche: *Bull. de la Soc. Chim. de France*, p. 66 (translation).

The presence of material quantities of sesquioxide in the phosphate rock is admittedly one of the principal causes of reversion. It is also known that pure superphosphates undergo a reduction of their water-soluble P_2O_5 , in consequence of the progressive hydrolysis of monocalcium phosphate, when they do not contain sufficient excess of free acid.

The possibility of a reaction between monocalcium and tricalcium phosphates cannot entirely be ruled out.

Wherever the necessary and sufficient conditions for the formation of a complex salt are found together in superphosphate, reversion will be observed as a consequence. Further, it has been pointed out by Sanfourche and his associates that temperature may exert a considerable influence upon the rhythm of evolution of a complex: this evolution reaches its limit the more rapidly higher temperatures are attained.

A few words should be said about the mechanism of drying solids.¹ In the initial stages of the drying of a very wet solid under constant drying conditions the surface is completely wetted with water, and the drying process is similar to the evaporation of water from a free liquid surface. As long as the surface of a solid to be dried is wholly wet the rate of evaporation is not a function of the water content of the solid, and, under constant drying conditions, the rate of drying continues constant. This stage is termed the *constant rate period*. However, at some definite water content the rate of drying begins to decrease and the range from there to dryness is called the *falling rate period*.

The water content of the solid at the end of the constant rate period, and the beginning of the falling rate period, is termed the *critical water content*. When dried for a long time the water content of the solid approaches an ultimate value which depends on the humidity of the air, and is termed the *equilibrium water content*. For further information concerning the constant rate period, heat conduction through dry surfaces and radiation from surroundings, it is suggested that the *Chemical Engineer's Handbook*² should be consulted.

Other factors to be considered are air velocity, and the effect of humidity. In connection with the falling rate period, this, in general, is divisible into two secondary periods, or zones, which from the mechanisms of drying prevailing in each may be called the zone of *unsaturated surface drying*, and the zone where internal liquid diffusion controls.

On the subject of air velocity it can be said that since the rate of drying during the constant rate period is controlled by the rate at which vapour can diffuse through the surface-air film, factors which affect the thickness of that film influence the rate of drying in this period. Perhaps the most important of such factors is the velocity of the air past the surface: the air velocity has a smaller influence on the rate of drying than it has on the surface coefficient of heat flow from solid to gas in air heaters and in similar equipment. Probably the best data concerning the relationship between the rate of drying and air velocity are those of Hinchley and Himus.³

With increasing appreciation of the causes of reduction and reversion, and in view of the availability of plant which admits of thermostatic control, there has been considerable development, within recent years, in the drying of calcium superphosphate, and many plants are operating in this country. This tendency has doubtless been stimulated by the fact that dried superphosphate emanating from abroad has found a ready market, because of the better drillability of such product. The Dutch Superphosphate Company dries the output of its works at Pernis, and the content of moisture of their superphosphate ranges from 2 to 4 per cent. By drying it is possible to convert 30 per cent water soluble superphosphate into one containing 35 per cent $Ca_3P_2O_8$. It should be noted that artificial drying, under controlled thermostatic conditions, admits of reaction between the free acid and the unattacked tribasic phosphate of lime, by which soluble P_2O_5 is produced. Incidentally, the free acid and insoluble phosphate are reduced with a correspondingly higher recovery efficiency.

¹ Lewis, *Ind. Eng. Chem.*, **13**, 427, 1921; Sherwood, *ibid.*, **21**, 12, 1929; **21**, 976, 1929; **22**, 132, 1930; and **24**, 307, 1932.

² McGraw, Hill Book Co., Inc., New York and London, 1934.

³ *Trans. Inst. Chem. Eng. (British)*, **2**, 57, 1924.

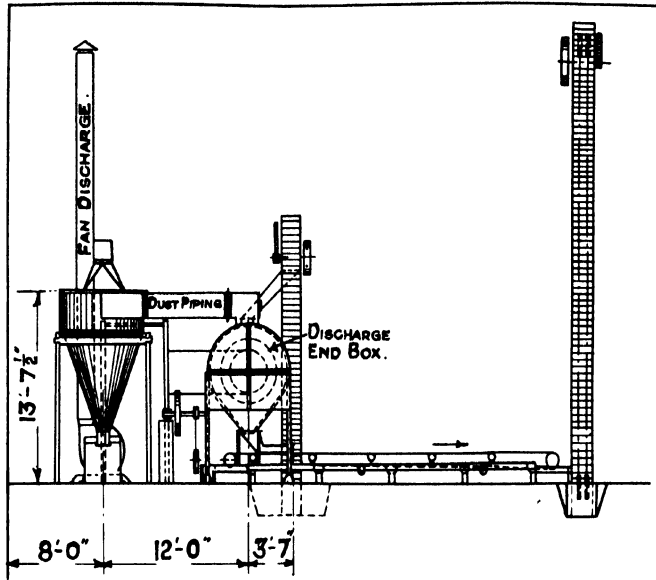
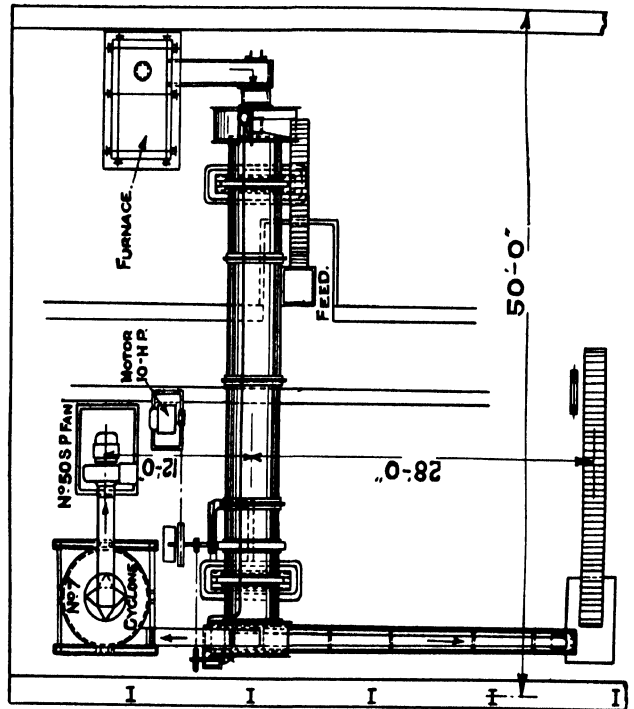
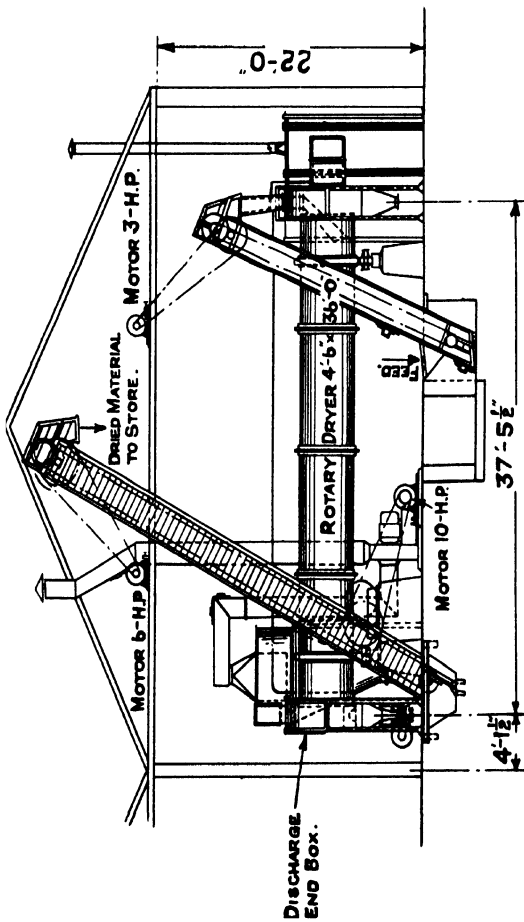


Fig. 58.—ARRANGEMENT OF STURTEVANT SUPERPHOSPHATE DRYING PLANT



The following table indicates the recovery obtained, additional to that due to the evaporation of moisture.

TABLE 24

Test No.	Moisture in Superphosphate.			Soluble P ₂ O ₅			Temperature in °F.	
	Inlet.	Outlet.	Loss.	Inlet.	Outlet.	Increase.	Exhaust gases at dryer outlet.	Super-phosphate as discharged.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		
1	15.5	9.08	6.42	13.68	14.76	1.08	142° F.	158° F.
2	15.5	6.80	8.70	13.56	15.01	1.45	152° F.	169° F.
3	15.8	5.6	10.8	13.85	15.6	1.75	178° F.	185° F.
4*	16.0	6.9	9.1	13.95	15.75	1.8	190° F.	205° F.
5*	15.5	4.8	10.62	13.85	15.85	2.0	190° F.	205° F.
6*	15.4	3.9	11.5	13.85	15.9	2.05	192° F.	212° F.

* In these three tests the theoretical increases in P₂O₅ content due to evaporation of water are 1.45 per cent, 1.65 per cent and 1.85 per cent respectively.

This indicates that further reaction between the free acid and the insoluble tribasic phosphate of lime had taken place within the dryer.

The illustration Fig. 58 shows a modern drying plant having a capacity of approximately 6 tons per hour of dried superphosphate. The feeding is undertaken by hand, as superphosphate is difficult material to feed automatically from a pile. In the case of a continuous den this difficulty is eliminated, as the dryer can be designed to dry the superphosphate at the same rate as the den discharges, without any man-handling whatever.

In the plant shown on Fig. 58, and drying at the rate of 6 tons per hour, receiving superphosphate containing 15 per cent moisture and delivering it with a moisture content of 5 per cent, the pre-war cost of drying represented:

	s.	d.
Coal at 46s. per ton	1	9
Labour	2	6
Power		3
Maintenance	1	6

Total 6 0 per ton dried.

It is usual in these drying plants to provide some form of thermostatic control. The simplest type consists of two electric lamps, one red and the other green. These lamps are interconnected with the thermostat, and when the temperature rises above a certain point the red lamp lights up, when the operator admits more secondary air; when the temperature falls below a certain point the green lamp lights up, which indicates to the operator that the furnace requires attention.

Oil firing is more expensive than coal or coke burning, but it lends itself to more accurate control and continuity of operation as there is no clinking or cleaning of fires.

The exhaust gases from the dryer contain from 0.3 to 0.6 per cent sulphur trioxide and tend to corrode quickly the ducting and cyclones, if made of thin sheet steel. It is a good plan to make all this work in asbestos acid-resisting material, which reduces the maintenance charges considerably, or the ducts should be lined with acid-resisting bricks jointed by special mastics, in which sodium silicate may form a part. It seems likely that the process of artificially drying calcium superphosphate may gradually fall into disuse, as the tendency in future years is likely to be in the direction of the granulation of superphosphate as a culminating unit operation in the production of an improved product, which may be demanded by the farmer very shortly.

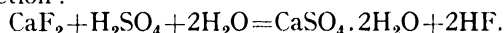
CHAPTER X

METHODS FOR DEALING WITH TOXIC GASES

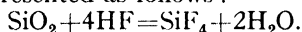
WHEN consideration was given to the chemistry of calcium superphosphate manufacture, it became evident that in the decomposition of mineral phosphates containing fluorides and other halogen bodies, such as chlorides and iodides, noxious gases would be evolved.

The toxic gases generated in the mixer and den during the manufacture of calcium superphosphate consist of carbon dioxide, hydrofluoric acid, hydrochloric acid, sulphur dioxide, and volatile organic compounds.

When calcium fluoride is present in a mineral phosphate, on treatment with sulphuric acid it undergoes the following reaction :



As most rock phosphates contain earthy matter there is invariably sufficient silica present to admit of the attack by hydrofluoric acid, which is released, as is indicated above. Thus, a further reaction proceeds, which may be represented as follows :



As, however, silicon tetrafluoride undergoes decomposition in the presence of water an additional reaction takes place, thus :



The action of hydrofluoric acid is not alone confined to silica, but complex silicates are attacked, and not less so the brickwork of the den.

As the mass undergoes reaction in the den it increases in temperature, steam is evolved, and as silicon tetrafluoride is also released, it is not unusual to find accumulations of the sponge-resembling silicic acid in the flues and connections, which have resulted from chemical reactions such as those just represented.

It must not be assumed that all the fluoride is completely decomposed. Chemists who have had occasion to investigate the extent to which decomposition of fluorides proceeds have found that the amounts released, and which remain unattacked, vary somewhat. This is doubtless due to the nature of the fluoride and the dissimilarity of the conditions obtaining.

It has been necessary in Great Britain for many years now to condense efficiently the noxious gases discharged during the manufacture of calcium superphosphate. Indeed, chemical manure works have been under the surveillance of the inspectors under the Alkali Works, etc., Regulations Act since 1881.

For many years the results of the alkali inspectors' periodical inspections have been incorporated in the Annual Report of the Chief Inspector. These records and observations are not only useful and interesting, but they constitute a criterion by which the progress of the industry in certain respects can be judged.

Without attempting to draw any progressive picture, a few random quotations will be made, and results will be indicated, in order to show not only the neglect which in the past occasionally occurred at some of the fertiliser works, but also to demonstrate how helpful these reports can be.

Mr. F. Napier Sutton, F.I.C., District Alkali Inspector, remarked in the report for the year 1909, p. 117 :

“No important change in plant or form of condensers has to be reported, with the exception of the installation at one of the largest works of a mechanical excavator for removing the superphosphate from the den. This particularly trying work was formerly done by hand labour, and it was accompanied by much discomfort from the presence of the hot and slightly acid vapours disengaged, and, moreover, there was danger from the falling mass of material, and accidents occasionally occurred. By hand labour it took a gang of five men eight to nine hours to clear a den of 60 tons; now a den of 80 tons of superphosphate is removed and delivered to a store by machinery under the control of one man in five hours.

" All mixing and condensing appliances have been maintained in effective condition, and the table on page 116 shows the acidity of the washed gases as discharged into the chimney or air from the wash-towers, together with the percentage of condensation effected." Again, in the year 1914, on p. 14, the Chief Inspector remarked :

" The extent of operations in this class of works was fully maintained during 1914, although there was a reduction of four in the total number of works registered as compared with 1913. This is the fifth year in succession that the number of works registered has suffered decrease, whilst throughout this period the importation of the chief raw material used—mineral phosphates—has uniformly increased.

" The use of mechanical means for dealing with the freshly prepared superphosphate was further extended. The numerous designs of plant for effecting this step in the process of manufacture offer a variety of choice to those interested, and should aid in the still further extension of this desirable advance in methods of production.

" The general condition of this class of works was maintained in a satisfactory state, numerous improvements and renewals being effected in the means provided for preventing escape of noxious gases into the air. The general average escape was equivalent to 0.112 grain of sulphuric anhydride per cubic foot—a satisfactory figure, although slightly higher than 0.105 grain, the corresponding figure for 1913."

TABLE 25

Average Amounts of Acid Escaping and Condensed

Register number of work and number of exit tested.	Total acidity in terms of the SO ₃ equivalent of Silicofluoric acid, H ₂ SiF ₆ ; grains per cub. ft.		Per cent. condensed.	Register number of work and number of exit tested.	Total acidity in terms of the SO ₃ equivalent of Silicofluoric acid, H ₂ SiF ₆ ; grains per cub. ft.		Per cent. condensed.
	Leaving mixer and den.	Leaving condenser.			Leaving mixer and den.	Leaving condenser.	
2124	6.17	0.23	96.2	2198	2.40	0.05	97.9
2129	10.90	0.10	99.0	2199 (a)	4.96	0.06	98.8
2130	1.74	0.05	97.1	2200	9.00	0.06	99.3
2152 (a)	8.10	0.15	98.1	2209	4.66	0.05	98.9
2190 (a)	5.25	0.08	98.4	2263	26.18	0.09	99.6
2190 (a)	9.37	0.08	99.1				
Average, 1909					8.07	0.09	98.9
Average, 1908					9.94	0.11	98.8

Further, in 1921 the Chief Inspector made some very pertinent remarks concerning condensing plants in their relation to the newer types of mixing plants, as well as concerning the position and speed of the draughting fan, which he regarded as a point of design still needing further consideration.

" *Chemical Manure Works.*—The average acidity of the gases escaping from scrubbing towers was considerably lower than that for 1920, which itself was lower than that for 1919. During the ten years—1910 to 1919—the average acidity of these gases was fairly constant; for that period it amounted to 0.118 grain per cubic foot, in terms of the SO₃ equivalent of H₂SiF₆, to which figure it had come down gradually from 0.2 in 1903. The gases evolved in the mixing process are by no means pleasant, and they are of a peculiarly corrosive character. Although the average figures could not be considered to be bad, it was nevertheless felt that further improvements might, and should be effected.

" A comparison of the results obtained in the various districts and in the individual works indicated an undue difference in some instances between maximum and minimum efficiency, and this pointed the direction in which action for improvement might best be taken. Absolute uniformity is difficult of attainment, especially where such considerable differences exist in the size and nature of the works as in this trade ; but much has been done already, and only one district shows this year an average exit acidity over 0.08 ; this district has had, however, only two superphosphate works operating, at one of which a badly designed scrubbing plant, recently erected, came in for severe criticism. This plant has now been entirely remodelled.

" In one district the activities of the inspector have resulted in the rebuilding of scrubbers, with a consequent reduction of over 50 per cent in the acidity of the escaping gases.

" With increasing introduction of the newer types of mixing plants, it is, however, more than ever necessary that manufacturers should take into consideration not only the acidity of escaping gases, but also the relation between the acidity of the gas evolved from the mixing plant and that of the gas actually escaping. Quantitative estimations indicate a removal of fully 97.5 per cent by the condensation methods employed. This is good, but there is still room for investigation with a view to further improvement. Condensing flues play an important part in removing a good deal of the noxious compounds, the amount of work to be done by the scrubbers being thus reduced.

" Mr. H. J. Bailey has carried out, at my request, a number of experiments at two works, with a view to ascertaining the efficiency of preliminary flues ; willing assistance was rendered by the managers and laboratory staffs of these works. The results obtained point to the fact that, with suitable flues, providing sufficient cooling of the gases, sufficient time contact, and suitable humidity, good preliminary work can be done.

" As to the nature and design of the scrubbing plant for chemical manure works gases, I may quote from Mr. Sutton's district report, in which he describes a very efficient arrangement, as consisting of three, four, or five unpacked tower chambers (according to the capacity of the mixing plant), each fitted with high-pressure water-sprays, these towers to be followed by two towers packed fairly closely with boards on edge, the direction of the boards in one layer being at right angles to that of the boards in the next layer. The two final towers are also supplied with water. The provision of the terminal packed towers is a point of considerable importance. The position and speed of the draughting fan are points which do not always receive sufficient consideration in the designing and operation of the plants."

Mr. W. A. Damon, B.Sc., Chief Alkali Inspector, speaking on Mr. Walter Packard's paper early in 1937, said he was interested especially in one aspect of superphosphate manufacture, namely, in dealing with the corrosive gases which were evolved. He thought it would be interesting to see what progress had resulted in the recovery of these gases. He therefore made an examination of the reports during the last forty-five years, and was pleased to find that there had been progressive improvement. The figures of acidity for the ten-year periods were as follows :

Up to 1890	0.46 grain per cubic foot
1900	0.37 " " " "
1910	0.23 " " " "
1920	0.12 " " " "
1930	0.07 " " " "
1930-1935	0.04 " " " "

The fact emerges that with any given rock phosphate, and with unaltered conditions, the proportion of fluorine evolved as SiF_4 is definitely a function of the concentration of the acid used. The higher the percentage of H_2SO_4 in the acid, the greater the evolution of silicon tetrafluoride. With the relatively dilute acid used for the decomposition of rock phosphate for the manufacture of phosphoric acid there is no evolution of silicon tetrafluoride whatever. That silicon tetrafluoride is first formed appears clear : but that the water present is so considerable that it is at once converted to hydrofluosilicic acid is equally clear. In the ordinary den process the silicon tetrafluoride is swept away from the reaction zone by the rush of carbon dioxide. Given time, as in the Oberphos process, it will react and form eventually calcium fluosilicate.

In 1936 the Chief Alkali Inspector's report emphasised the need for a "delay period." For this reason a connecting flue of some length, or otherwise a large void chamber, suitably constructed, should be provided.

The reason for the "delay period" is not far to seek, when one has regard to the time required for the decomposition of the silicon tetrafluoride. Early wetting and cooling of the gases, succeeded by an "adequate delay period," to admit of decomposition of the silicon tetrafluoride being completed, is essential. Hitherto it does not appear to have been generally recognised that the decomposition of SiF_4 (silicon tetrafluoride) to silica and hydrofluosilicic acid by the action of water requires some time. This object may be attained by the erection of scrubbing towers at a distance from the dissolving plant, and by conveying the gas in a long flue. Where this is not possible, previously wetted gas must pursue a tortuous course through a chamber, to admit of time for the reaction to take place. Most of the silica is deposited in the "delay chamber," from which it can be removed.

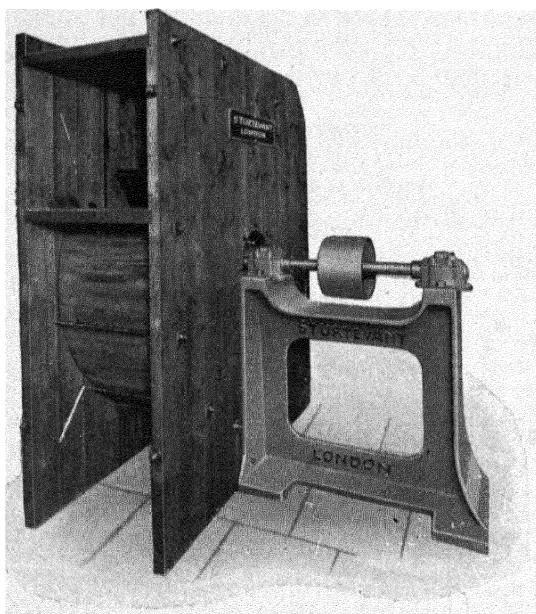


FIG. 59 ACID FUME FAN

The "dry and wet method" of treating gases will be the subject of detailed treatment later. At this juncture it is desirable to give some data relating to the treatment of the gases from the mixer and den in connection with intermittently operated superphosphate plant. The Chief Alkali Inspector, Mr. W. A. Damon, B.Sc., has had a wide experience of various plants in this connection, and has been keen to reduce the escapes to negligible acidities. The system which he strongly advocates for a plant of a capacity of 30 tons of superphosphate per hour is indicated succinctly below.

(1) The gas should be drawn from the mixer and den through a wooden or concrete duct to a tower, in which it is thoroughly cooled and wetted by means of high-pressure water sprays. The capacity of tower, or towers, should be of the order of 700 cubic feet.

(2) The cooled and moist gas should then pass to a "delay chamber." This should consist of a tower provided with horizontally placed baffles, so as to cause the gas to pursue a tortuous path, in a cross-section of 8 feet square for a total travel of some 100 feet. Silica settles out on the baffles, and trays should be provided, to allow of its easy removal.

(3) The gas should then be washed in a series of void towers provided with water sprays. A total capacity of 1500 cubic feet may be allowed with advantage.

(4) The fan is placed at the end, so as to deal with clean gas, and to keep the whole system under a slight suction. If possible, the discharge should be into a high and hot chimney.

In many works it is necessary to provide a simple scrubbing tower for dealing with fumes from the den during the cutting-out process. The fumes consist mainly of steam, with very little acid.

Practice reveals that the fan is best disposed after the condensing tower. Thus the gases are under suction throughout their travel of the whole condensing and scrubbing plant.

The fan (see Fig 59) is built of wood, coated with a suitable preservative to counteract the action of the acid fumes. It is usual to run it at a comparatively low speed, of approximately 400 revolutions per minute.

The dry and wet method of treating the gases is shown in Fig. 60. In this arrangement the fan is placed between the dry and wet chambers, the gases are drawn through the dry chamber, and immediately they enter they expand, owing to the increased area, and their velocity is considerably reduced.

This causes the solid matter, held in suspension, to separate and fall on the floor. This dry chamber is built with a series of partitioned walls, so that the gases are travelling down and up several times before they reach the fan. These partitions act as baffles, and assist the separation of the solid matter. Doors are provided in each partitioned portion for the removal of the deposited silicious dust.

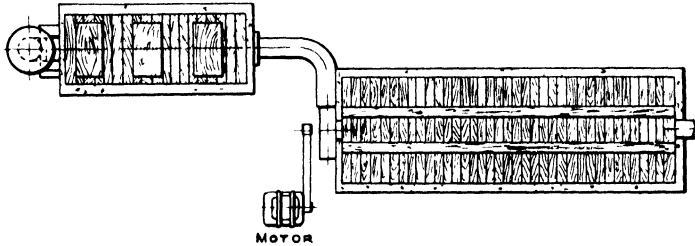
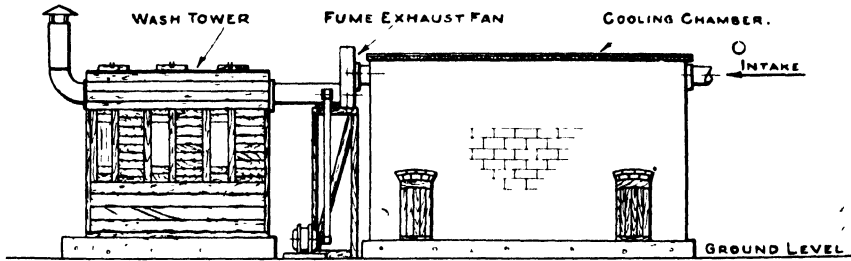


FIG. 60.—TOXIC GAS CONDENSING CHAMBERS

The fan discharges the partially cleaned gases into a second or wet chamber. On top of this chamber is mounted a series of water-sprays. This chamber is also divided into partitions, and each section is divided horizontally by trays of splay boards. Here again the gases travel down and up several times, and during their progress are thoroughly washed by the spray showers which they have to encounter in their passage.

The remaining solids in the gases, when they enter the second chamber, are precipitated by the action of the water, and the gases, free from obnoxious matter, are either exhausted into the atmosphere or, if convenient, into the works chimney.

The advantage of the dry chamber is that it separates most of the solid matter and relieves the

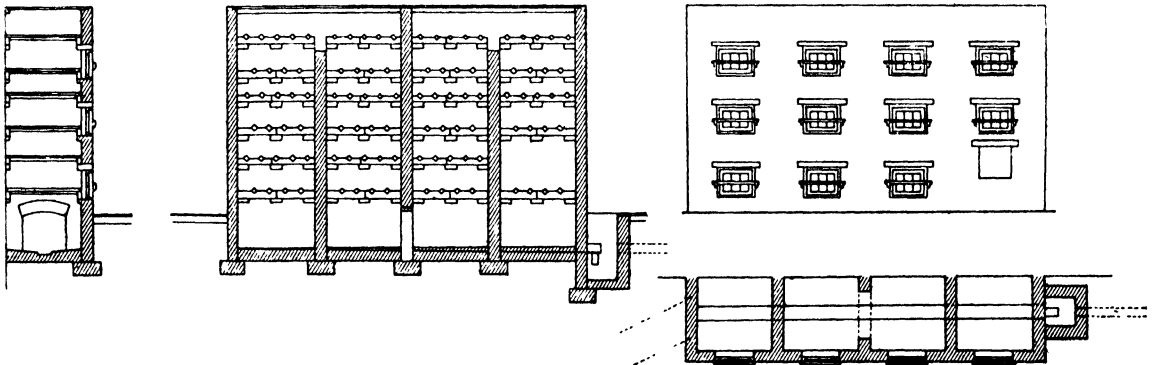


FIG. 61.—TOXIC GAS CONDENSING CHAMBERS (WET CHAMBERS ONLY)

condensing chamber of considerable work. Less water is required in consequence, and sometimes this is a great consideration. Twenty-five gallons of water per minute are usually sufficient.

Fig. 61 shows that system when a wet chamber only is used. This is usually built of brickwork with a glazed facing inside. The gases are drawn through the chamber, so as to protect the fan from the solid matter. In this arrangement greater resistance is created, and the fan must be larger and more power is absorbed in overcoming the additional resistance.

In the United States of America the condensing chambers are, in many instances, constructed of wooden cylinders, made in sections with spigot joints and screwed iron rods clamping the joints.

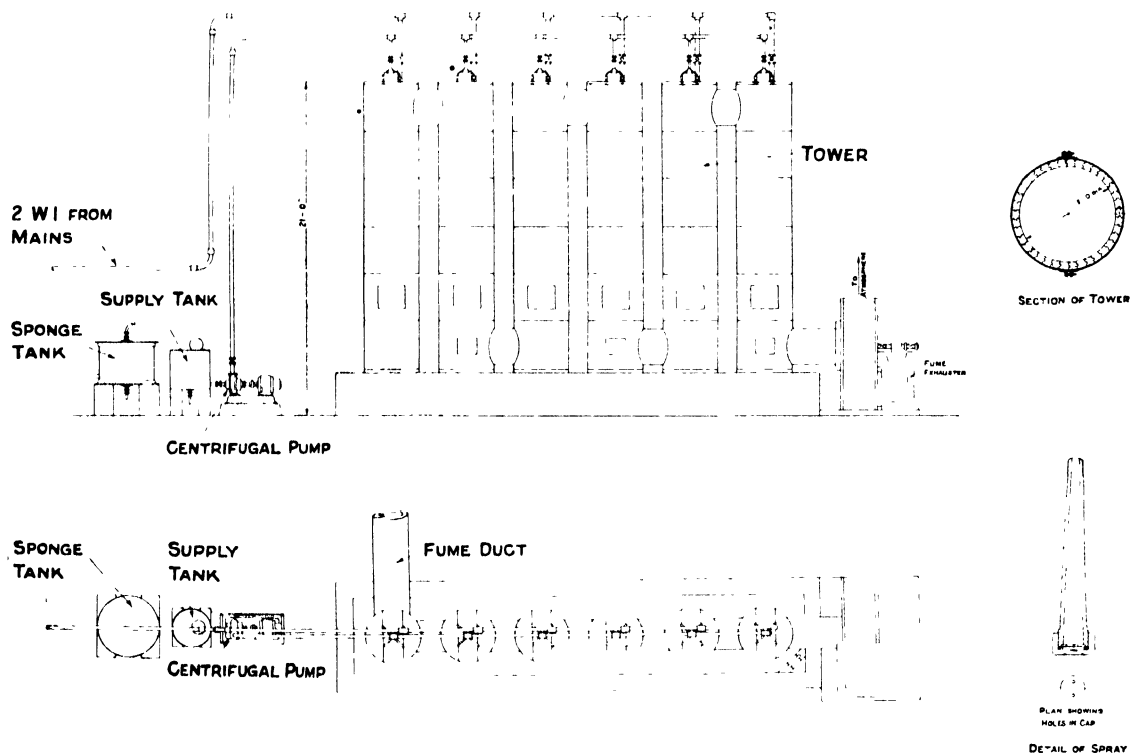


FIG. 62.—CONDENSING TOWERS USED IN U.S.A.

They are usually 3 feet inside diameter, and vary in height. A fan is placed at the end of the towers and the gases pass upwards and downwards through the towers. In their progress the gases are thoroughly washed with atomised water. The sprays are disposed in the towers at different levels. These towers stand on a concrete base, as shown in Fig. 62.

The Kestner system of washing the toxic gases is shown in Fig. 63. It consists of a series of rotary atomisers. These impart centrifugal force to fine streams of water, which are delivered in front of the atomising mechanisms. The gas chamber shown in Fig. 63 has six of these atomisers distributed along the length, three on each side.

8 seconds, and the velocity through the scrubbers should not exceed 10 linear feet per second. The amount of water required for spraying should not be less than 150 gallons per ton of superphosphate produced per hour. As an example, take a continuous den producing 10 tons per hour of superphosphate.

The volume of gas to be dealt with is :

$$\begin{aligned} 1300 \text{ M}^3 \times 10 &= 13,000 \text{ M}^3 \text{ per hour,} \\ &\text{equivalent to 7600 cub. ft. per minute,} \\ &\text{or 127 ,, ,, second.} \\ \frac{127}{10} &= 12.7 \text{ sq. ft. area of scrubbing towers.} \end{aligned}$$

Therefore, the dimensions of the towers should be 4 ft. \times 3 ft. 3 ins, and the length 10 ft. \times 8 sec. = 80 ft.

Thus, one would make provision for the construction of five towers of 16 ft. height, or four towers of 20 ft. height, according to local circumstances and wishes.

The Production of Saleable Sodium Silicofluoride

The gases—silicon tetrafluoride, steam, and hydrochloric acid, etc.—from the superphosphate den and mixer are withdrawn, as has been described, and led to a condenser A, which is provided with a series of water atomisers.

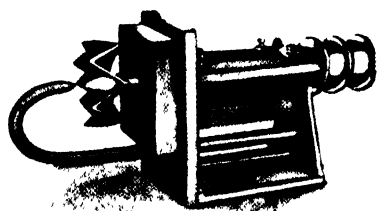


FIG. 64.—KESTNER ATOMISER

According to tests which the authors have made, it is found that when 99.5 per cent recovery of the acid gases is being effected with a normal supply of water (not circulated), the acidity of the water reaches about 4 per cent, expressed in terms of H_2SiF_6 .

Wherever it is proposed to recover the hydrofluosilicic acid as sodium silicofluoride, it is obvious that the water should be maintained in circulation through a given condenser, in order that a suitable concentration should be reached.

This is effected in the scheme illustrated in Fig. 65 by circulating the acid solution from tank B, through the condenser A, to tank C, until a specific gravity of 1.082 (i.e. 10° Bé.) is reached.

The next step is to introduce the solution of the specific gravity named to a settling tank, where the solid matter, largely silicic acid (H_4SiO_4), is allowed to separate, and can subsequently be removed. Meanwhile, the clear liquid, consisting of hydrofluosilicic acid, etc., is transferred to a precipitating tank E.

From tank F is run a brine solution, having a specific gravity of 1.18 (22° Bé.), representing about 23½ per cent NaCl, to the clear acid liquor in a precipitating tank, until the whole of the hydrofluosilicic acid has been converted to sodium silicofluoride, as determined by a laboratory test.

At one works it has been found that the proportions have been one of brine to three of acid solution.

It will be appreciated that if the acid solution contains any appreciable quantity of sulphurous acid, due to the absorption of SO_2 in the water circulated, sodium chloride will be consumed to no useful purpose. This is a consideration which needs to be taken into account when forming an idea of the desirability of recovering fluorine from mineral phosphates as sodium silicofluoride. Equally the question of the fluoride content of the rock phosphate, and the extent to which this is recoverable as sodium silicofluoride, should be considered.

It is conceivable that a good deal of the original fluorine may escape, due either to volatilisation or to imperfect hydrolysis, or to other causes. These factors should be investigated at the superphosphate works before deciding upon the installation of a plant for the recovery of the fluorine as sodium silicofluoride.

Following the precipitation of the hydrofluosilicic acid as sodium silicofluoride, which latter takes the form of a snow-like salt, the weak liquor, consisting largely of dilute hydrochloric acid, is run off, and the precipitated salt is centrifuged in the centrifugal G. It is important that the salt should be thoroughly washed, in order to remove the whole of the free acid.

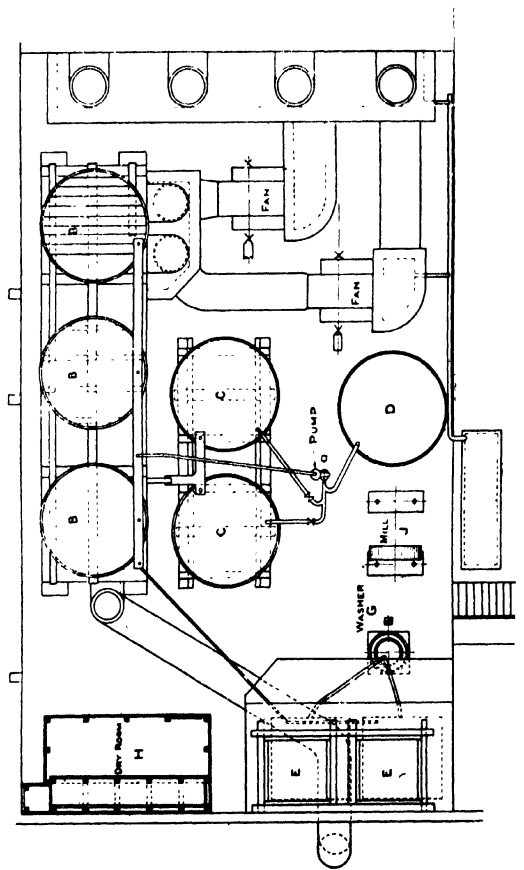
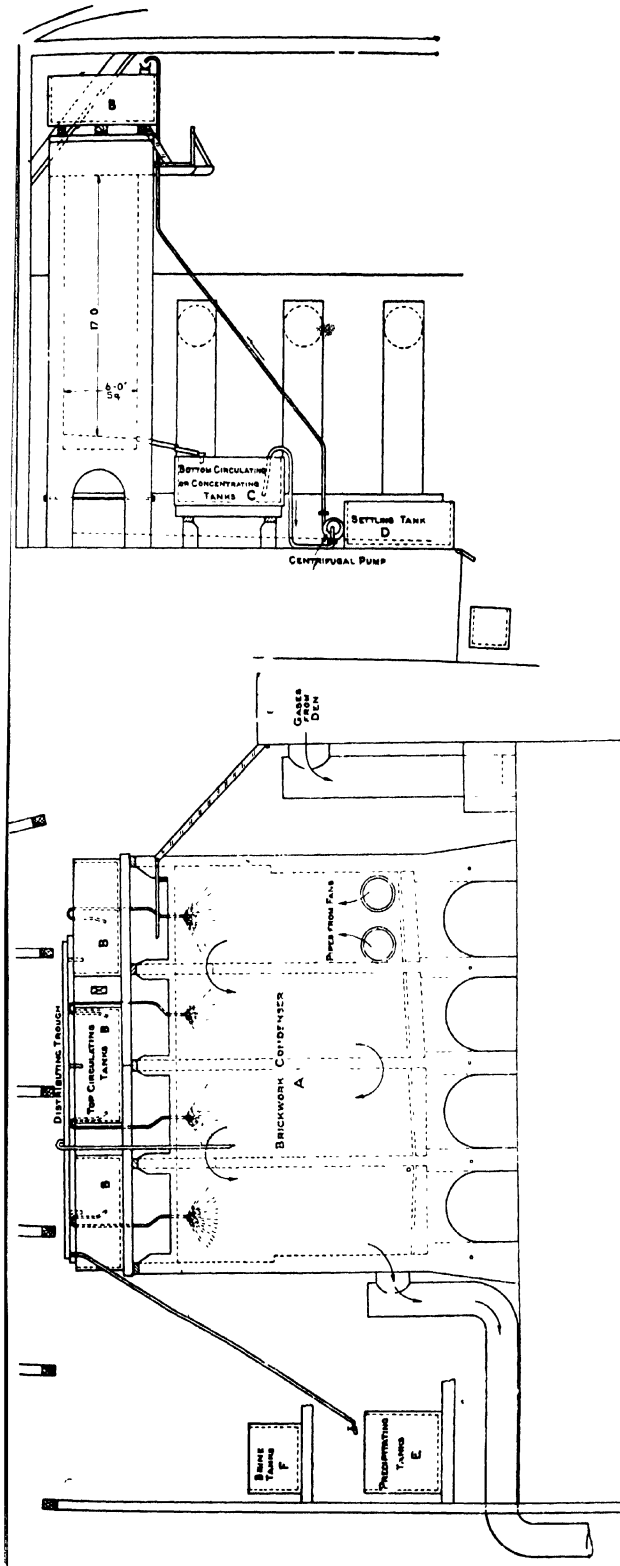
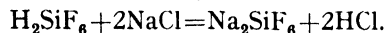


Fig. 65.—CONDENSER FOR RECOVERY OF HYDROFLUOSILICIC ACID

The formation of sodium silicofluoride from hydrofluosilicic acid may be represented as follows :



After the precipitated salt has been washed it is next placed in suitable trays, and these are put into a suitable drying cupboard H, which is steam-heated.

Following the drying operation, the salt is ground in a small batch grinder J, lined with porcelain, and having flint pebbles. It is ground to a fine powder, and is then ready for sale.

From a plant with which the authors are acquainted, producing 1000 tons of "super" per week, approximately 2 tons of sodium silicofluoride were recovered per week, representing about 4.5 lb. per ton of "super."

The above figures relate to a works using North African mineral phosphates, which are low in silica.

In America, Florida and other phosphates are very high in silica, and this accounts for the higher recovery figure of 8.5 lb. per ton of "super."

Indeed, it is due to the better recovery that one finds more of these plants operating in America than in Europe.

Taking the CaF_2 content of a mineral phosphate at 2.55 per cent—a low figure—and taking a mixing of 10 cwt. of ground phosphate rock and 9.25 cwt. of acid of 114°Tw. at 100°F. , and assuming the yield of "super" to be $17\frac{1}{4}$ cwt. from such a mixing, the following data are arrived at :

- (a) Seventy-eight parts of CaF_2 (calcium fluoride) = 62.66 parts of sodium silicofluoride (Na_2SiF_6).
- (b) In 10 cwt. of phosphate rock, having 2.55 per cent CaF_2 , there are 28.56 lb. of CaF_2 , representing about 23 lb. of Na_2SiF_6 .
- (c) Hence the quantity of Na_2SiF_6 from 1 ton of "super" will be— $17.25 : 20 :: 23 : x = 23.65$ lb. of sodium silicofluoride.
- (d) If only 4.5 parts are recovered, it is seen that the efficiency of recovery is only 17 per cent.

It will be appreciated that a sodium silicofluoride plant is expensive in the matter of maintenance, as one has to deal with a corrosive acid liquor. Lead pipes are destroyed, as indeed are other metals which come into contact with the acid liquor. The only material which is resistant to its action is glass earthenware.

The men operating the plant must wear rubber gloves, and must exercise care in order to avoid acid splashes on any part of the skin.

One man, with occasional help, can operate a 2-ton per week plant. Table 26 shows details of the operation of a plant using Florida phosphate for two distinct periods, from which it will be seen that the recovery of sodium silicofluoride was 16.5 lb. per ton of rock phosphate acidulated during one period, and 18 lb. of sodium silicofluoride per ton of rock phosphate acidulated during the other period. Manufacturing and repairing costs per lb. of sodium silicofluoride are also given in decimals of a penny.

The economic value of the hydrofluosilicic acid—the residue which results from evaporation of the liquor from the settling tank—is dependent upon the cost of such evaporation.

TABLE 26
Sodium silicofluoride plants—working costs

Plant.	Number of working weeks.	Lb. of sodium silicofluoride made.	Yield: lb. per ton of rock dissolved.	Labour cost in pence per lb. sodium silicofluoride made.		
				Manufacturing.	Repairs.	Total.
A.	9	55,350	19.18	0.567	0.27	0.837
B.	10	90,250	14.75	0.525	0.12	0.645
C.	10	36,470	13.60	0.600	0.07	0.670

✓ CHAPTER XI

TREATMENT AND STORAGE OF SUPERPHOSPHATE

THE design and mechanical equipment of the storage buildings in fertiliser works are both very important. On account of the large quantities of material annually passing through the factory, facilities for rapid handling should receive first consideration. The amount of storage has then to be determined. Superphosphate forms the largest bulk of the materials to be stored, and in order that it may be thoroughly matured before dispatch, it generally lies in the store several months after it is made. With the recent qualities of superphosphate made by the Broadfield, and especially the Oberphos process, there is no necessity to store for more than a few days.

In the European factories storage is inevitable in any case, owing to the seasonal aspect of the trade. During the autumn months there are comparatively few sales. Hence almost the entire production during this varying period has to be stored until the busy season in the late winter and early spring.

The usual storage provided is 10,000 to 20,000 tons of superphosphate in a works of average size, representing 35-40 per cent of the total output. In the largest factories 30,000 tons or more are generally accommodated.

There is usually storage room for half these quantities of raw phosphate respectively.

In the United States of America, buildings equipped with travelling cranes are most popular. The crane-type building, as it is called, allows an overhead travelling crane to run from end to end, which is used for handling all the goods in and out. In some of the factories the crane is also used for excavating the dens, as described in Chapter VI. Such cranes generally have a total lift of

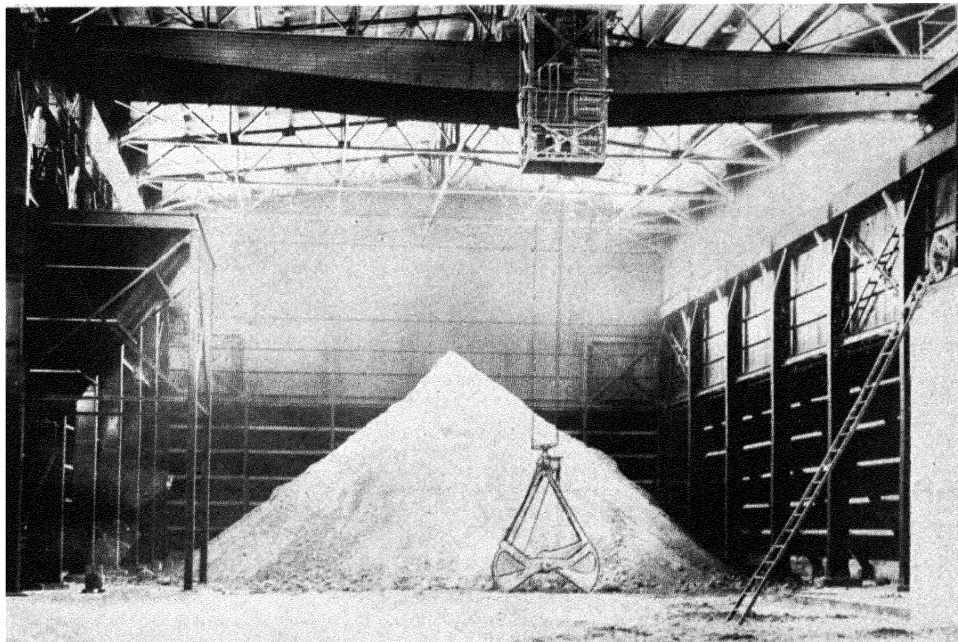


FIG. 66.—CRANE TYPE BUILDING FOR SUPERPHOSPHATE

about 45 feet, a span of approximately 75 feet, and a travel of about 450 feet. The grab bucket is usually rated to carry 30 cwt., but can handle loads up to 35 cwt. The power of the motors which operate the various movements totals approximately 100 h.p. These cranes are equipped with electrical braking devices, and can be controlled with ease and accuracy. It is not difficult for one of these overhead cranes to handle 400 to 500 tons of material per day, work which hitherto involved the employment of thirty men.

In large works this system of handling materials has proved very economical, and it is beginning to be adopted in Europe. Two factories in England are now operating this system. A building of the crane type is shown in Fig. 66.

The span is usually from 75 to 100 feet. The supporting columns and framework are made of steel sections, and the covering on the roof and sides is either galvanised iron or asbestos sheeting.

The overhead travelling crane enables large quantities of bulk materials to be handled in an expeditious manner. It is efficient both in filling and emptying the building, as all the ground area can be reached by the crane bucket.

A design which obviates any bursting pressure acting on the side walls is shown in Fig. 67. At one or both sides of the building a lean-to is arranged, which allows the heap of superphosphate to assume its natural angle of repose. An external view of a similar design is shown in Fig. 68.

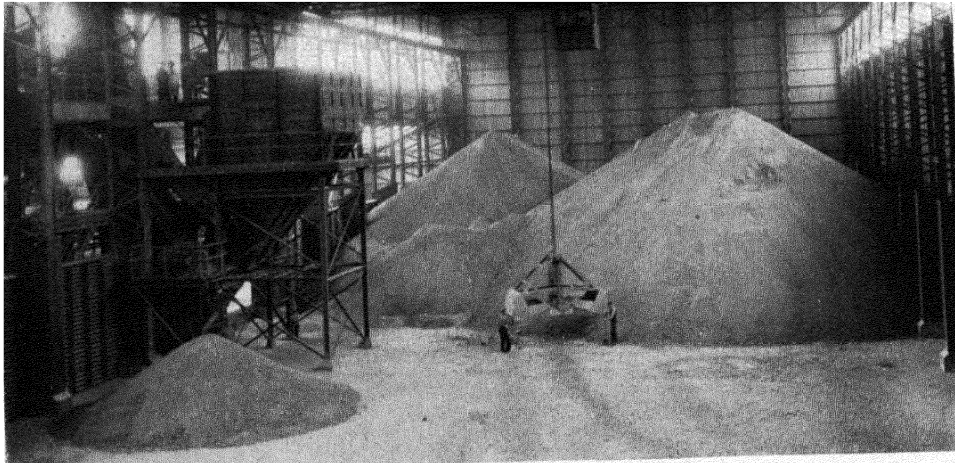


Fig. 67.—BUILDING WITH LEAN-TO SIDES

The overhead travelling crane makes it convenient to arrange the compound mixing and shipping units along one side of the building, as seen in Fig. 86. The goods for dispatch are also loaded into trucks on this side; there is a raised platform, level with the truck floor, and as the bags are filled, they have only to be wheeled along to the truck. Fig. 68 shows the loading platform.

This type of storage building cannot be surpassed, where large quantities of superphosphate and other fertilisers have to be moved quickly in and out of the factory. Large hourly tonnages can be handled very cheaply with one man operating the crane.

Another type of storage building, which is common to all countries, is known as the A frame building. This type is sometimes constructed of steel and sometimes of timber.

Fig. 69 shows the section of a steel A frame building and Fig. 70 shows one made of timber.

With the A frame construction there is no pressure on the side walls, as the angle of the framework practically coincides with the natural slope of the pile of superphosphate.

Near the apex of the A frame a continuous gantry extends from end to end of the store. The superphosphate is elevated at one end of the building and delivered to trucks at this level; these trucks, which usually hold two tons, are operated by a winch and wire rope. When the truck is

filled it is pulled out along the gantry, and, on reaching a predetermined point, the side doors automatically swing open and the contents fall into the store. The winch is reversed, and the truck returns for another load.

A very suitable truck for this duty is shown in Fig. 71.

Another method employed for dumping the superphosphate in this form of building is to convey it overhead in skips running on a monorail. These skips are electrically operated, or mechanically operated by means of a winch and wire rope, and trip gears are arranged for the skips to discharge at any point required.

Fig. 72 shows an A frame building with the gantry overhead and the superphosphate pile in the foreground. This shows very clearly the absence of any side pressure due to the pile. This type of storage building can be economically filled, leaving very little waste space, but there is no practical means of emptying it, except by "navvy" excavators filling into electric trucks.

Fig. 73 shows the large superphosphate store at the Vlaardingen Works, Holland. The superphosphate is conveyed to the store by means of an electric monorail suspended from the roof ties. Bakema portable bagging machines are used for excavating the pile.

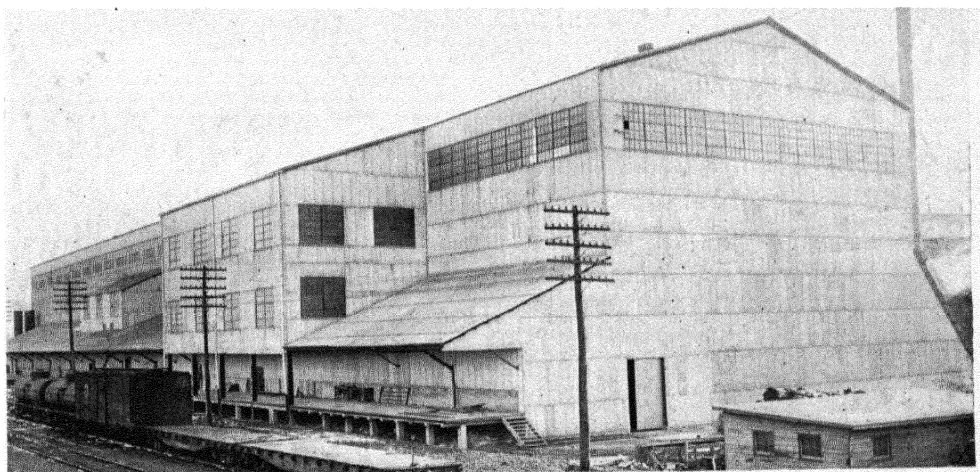


FIG. 68.—EXTERNAL VIEW OF BUILDING WITH LEAN-TO SIDE

Another type of store is illustrated in Fig. 74. The walls are built of brickwork, and the roof principals are made of timber designed on the Belfast principle. The roof covering is Ruberoid laid on timber.

This store is filled by means of an endless ropeway operating a series of skips. At a point in the store where the superphosphate is delivered from the mechanical dens, there is a loading platform. The skips are pushed under the hopper above and take their load, the operator then clips them to the wire rope, and they start off on their journey. Tipping gear is arranged at various points, and when a skip has been emptied it continues its journey round the store and back again to the loading platform. Sufficient skips are provided, so that as soon as one is filled another is ready to take its place under the hopper.

Sturtevant portable bagging machines are used here for excavating the pile.

Tray conveyors are also used for depositing the superphosphate in the store, and the "tip-tray" conveyor, made by Babcock & Wilcox, is a very suitable type.

Fig. 75 shows one of these conveyors in elevation. The trays are mounted on pivots between two strands of chain. At convenient points along the length of the store trip gears are fixed, so that as each tray passes any of these gears set to trip, it is automatically tipped, and returns to its original position.

This type of conveyor has several advantages: it delivers the superphosphate in a more or less even stream, it discharges at convenient points without any rubbing of ploughs, and is entirely automatic in its action.

In storage buildings which are not provided with overhead cranes, various mechanical devices are employed for excavating the superphosphate.

One of the most powerful machines employed for this purpose is the Thew shovel, illustrated in Fig. 45. It is designed to work under the handicap of low overhead clearances, around and

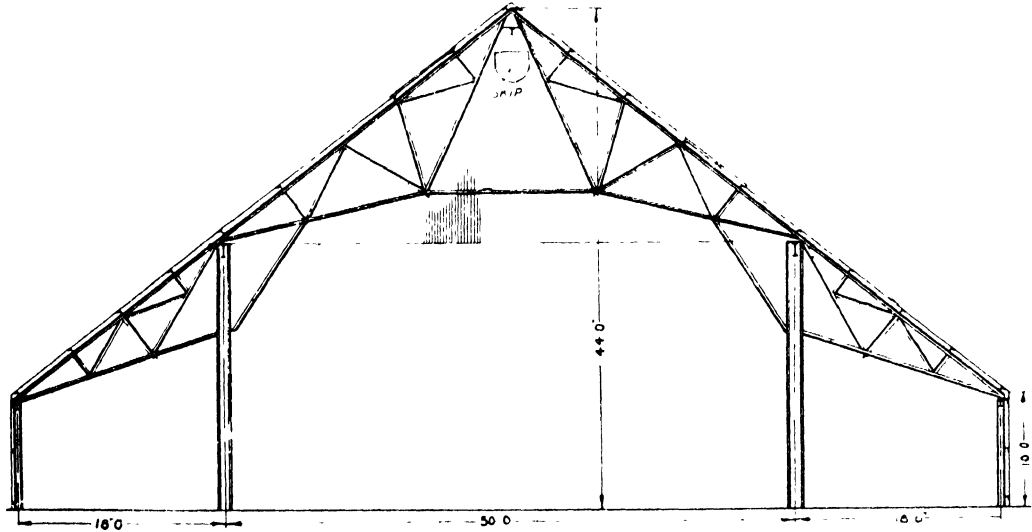


FIG. 69.—STEEL "A" FRAME BUILDING

between posts. Such conditions are often found in the majority of fertiliser works. It is operated by steam or electricity, and breaks down the hardest compounds without the slightest difficulty. One of these shovels will do the work of approximately twenty men. It usually operates with a train of storage battery trucks, as shown in Fig. 116.

The Jeffrey digger and loader is illustrated in Fig. 76 and is also used for digging superphosphate from the pile and delivering into trucks or barrows. It consists of an elevator mounted on a chassis in such a manner that it can be adjusted to any angle to suit the cutting or the loading. The buckets are made of malleable iron, and have a renewable steel digger edge, riveted round the front and a portion of the sides. Digger tools are spaced at intervals between the buckets, which loosen the superphosphate, and also tend to protect the buckets. The machine is rugged and massive in detail, and the whole of the driving mechanism is operated by a 7½ h.p. motor. It has a capacity of 60 tons per hour when fed continuously, and one man can operate the machine.

Superphosphate, excavated by the machines described, requires to be pulverised or screened before it is suitable for bagging to send out. It should all pass a ¼-inch sieve. In the handling

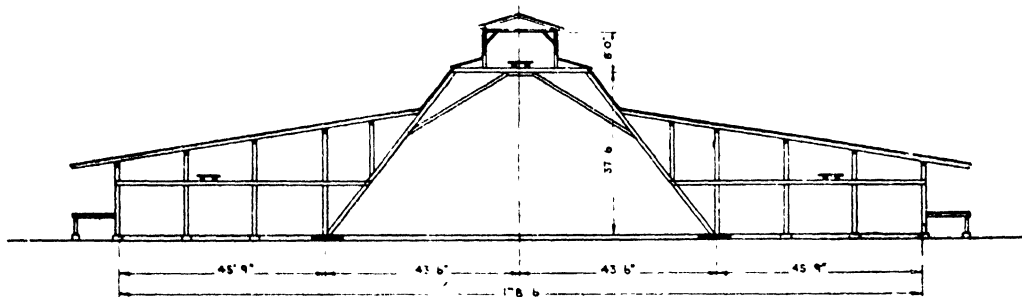


FIG. 70.—"A" FRAME TIMBER BUILDING

it receives when being excavated, a large proportion is reduced to $\frac{1}{4}$ -inch size, but the remainder has to be pulverised.

Two types of plant are used for this purpose—one stationary, the other portable. Stationary plants have a larger capacity and are usually situated adjacent to the loading stage, so that the dressed material when bagged can be put on rail with a minimum of handling. The superphosphate is brought from the pile to the dressing plant by crane, truck, conveyor, or other means.

A typical stationary dressing plant is shown in Fig. 77.

The superphosphate, which is shown being excavated by a digger, is brought in barrows or trucks and tipped into an elevator hopper. It is elevated to an inclined vibrating screen of special design, which is described later. The "fines" which pass through the screen are collected in a bagging hopper underneath and the tailings are by-passed to a small pulveriser, which delivers its products again to the elevator and over the screen a second time. In this way nothing enters the bagging hopper which has not been properly graded. Weighing scales are attached to the spouts of the bagging hopper and the sacks are weighed off as they are filled.

Fig. 78 shows the Lanvermeyer excavating and bagging machine. It is a powerful apparatus and the latest models are equipped with caterpillar chains which enable the machine to be moved over rough or uneven floors. It will cut the hardest manures direct from the heap and thus avoids blasting or the use of compressed-air drills to break down the mass. It combines an elevator with buckets staggered as shown in the illustration and secured to six sets of chains, a vibrating screen, a double roll crusher having toothed and smooth faces, and a rubber-faced belt for delivering the finished material to the bagging hopper at the end of the machine.

The manures are delivered by the elevator to the vibrating screen, the fine material which passes through the screen falls on to the belt conveyor, and the oversize goes forward to the crushing rolls. The latter machine delivers the crushed product to the same conveyor.

The caterpillar chains hold the machine securely in place against the working pressure, particularly if the manures have set hard.

It has a capacity of approximately 20 tons per hour and requires 30 h.p. for driving.

All parts are accessible and a walking platform is arranged on top with an access ladder from the ground level. The machine stands approximately 15 feet high and the working face of the elevator is 25 feet.

The Sturtevant excavating and bagging machine is shown in Fig. 79. It consists of an elevator of heavy design, which delivers the superphosphate to an inclined vibrating screen. The fine material passes through the screen, and is collected in a two-way hopper with bagging spouts. The hard cores, or tailings, are fed to a pulveriser, which reduces them, and this material is again elevated to the screen, to ensure that the whole of the material is correctly graded before bagging. The screened product is delivered on both sides of the machine, and bagged from two bagging spouts fitted with control valves. This machine may be fitted with a two-armed sack-weighing scale, or the bags may be weighed on ordinary platform weighing scales. The capacity of the apparatus is 8 to 10 tons per hour, and 10 h.p. is required for operating the several machines comprising the unit. It is easily portable, and all parts are accessible. Manures can be dressed, bagged, and weighed in a machine of this type at a cost for labour of 8d. per ton.

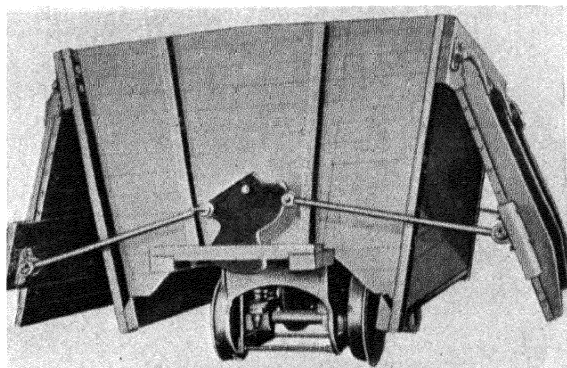


FIG. 71.—SUPERPHOSPHATE DUMPING CAR



FIG. 72.—“A” FRAME BUILDING SHOWING PILE OF SUPERPHOSPHATE



FIG. 73.—SUPERPHOSPHATE STORE AT VLAARDINGEN, HOLLAND



FIG. 74.—SUPERPHOSPHATE STORE BUILT IN BRICKWORK

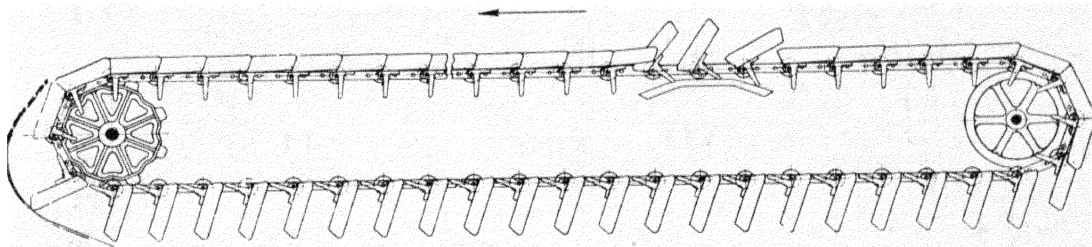


FIG. 75.—BABCOCK TIP TRAY CONVEYOR

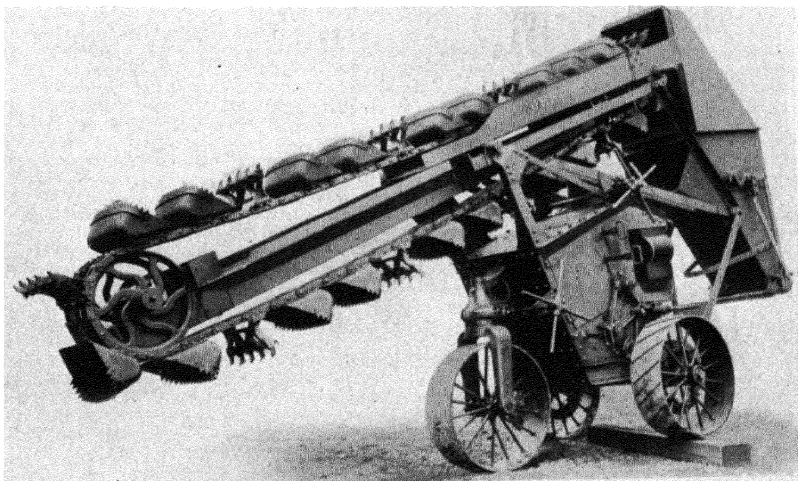


FIG. 76.—JEFFREY DIGGER AND LOADER

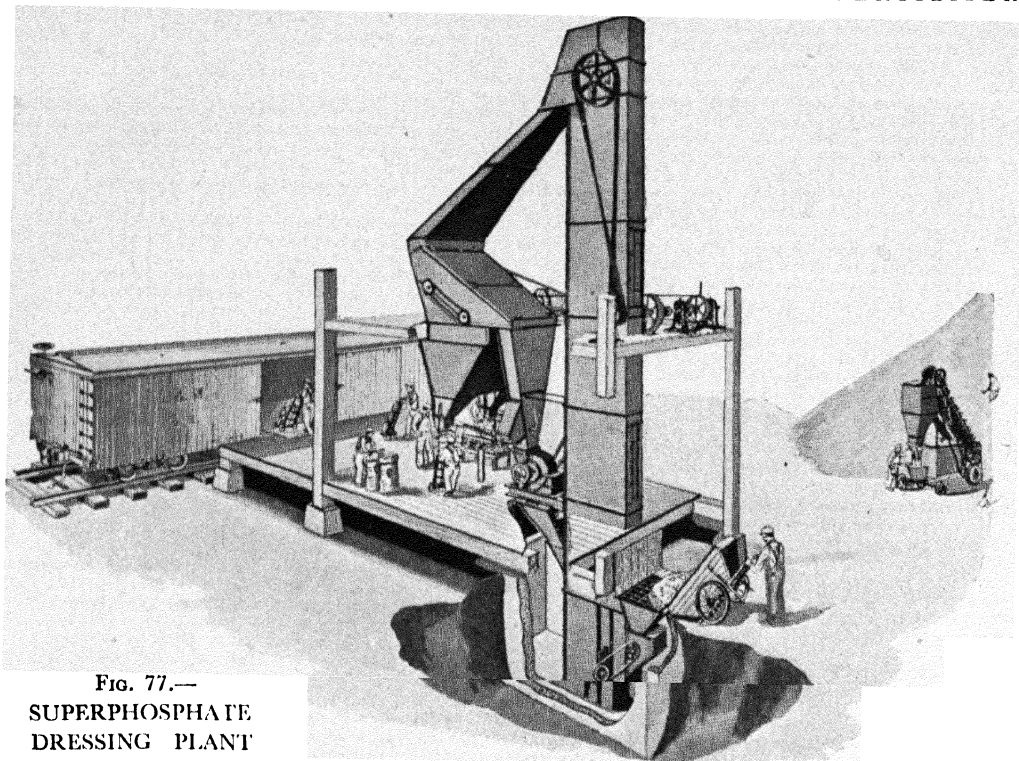


FIG. 77.—
SUPERPHOSPHATE
DRESSING PLANT

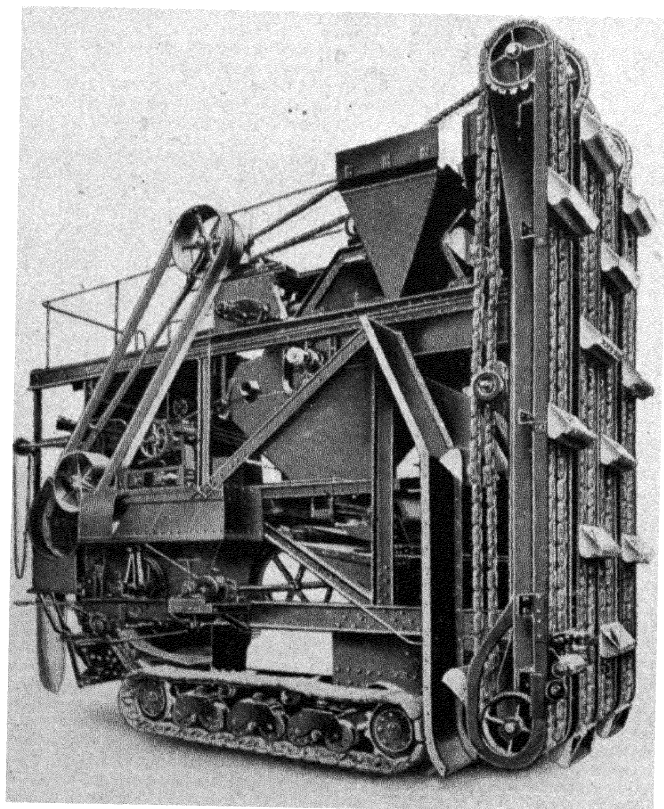


FIG. 78.—
LANVERMEYER
EXCAVATING AND
BAGGING MACHINE

Christy & Norris Double Rotor Machine for Superphosphate.

This type of pulveriser is particularly suitable for dressing the superphosphate made by the Oberphos process. As previously mentioned, this system produces a hard, gritty superphosphate and approximately 66 per cent has to be pulverised before dispatch.

The machine is illustrated in Fig. 80 and embodies one rotor with swing hammers running at approximately 1500 revolutions per minute, and a second rotor in the form of a slow-speed drum, against which the material is driven by the hammers.

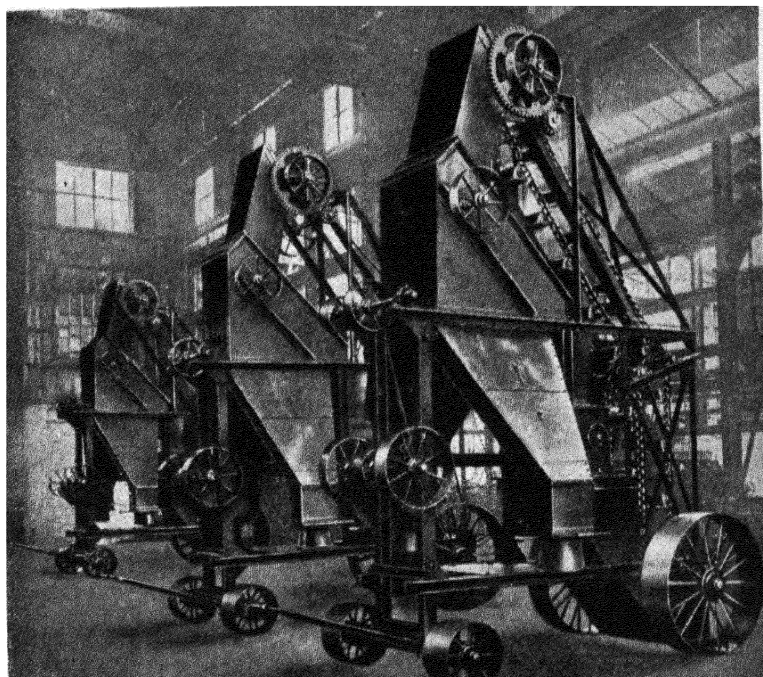


FIG. 79.—STURTEVANT EXCAVATING AND BAGGING MACHINE

The face of this drum is convex and does not allow the superphosphate to cling tightly and is practically self-cleaning, although scraping with a shovel, which takes only a few minutes, is advisable every few hundred tons.

These machines are made in two sizes. One, 24 in. \times 24 in., will handle 18 to 20 tons per hour and requires 35 h.p. to drive it. The other, 24 in. \times 36 in., will handle 30 tons per hour and requires 50 h.p. to drive it.

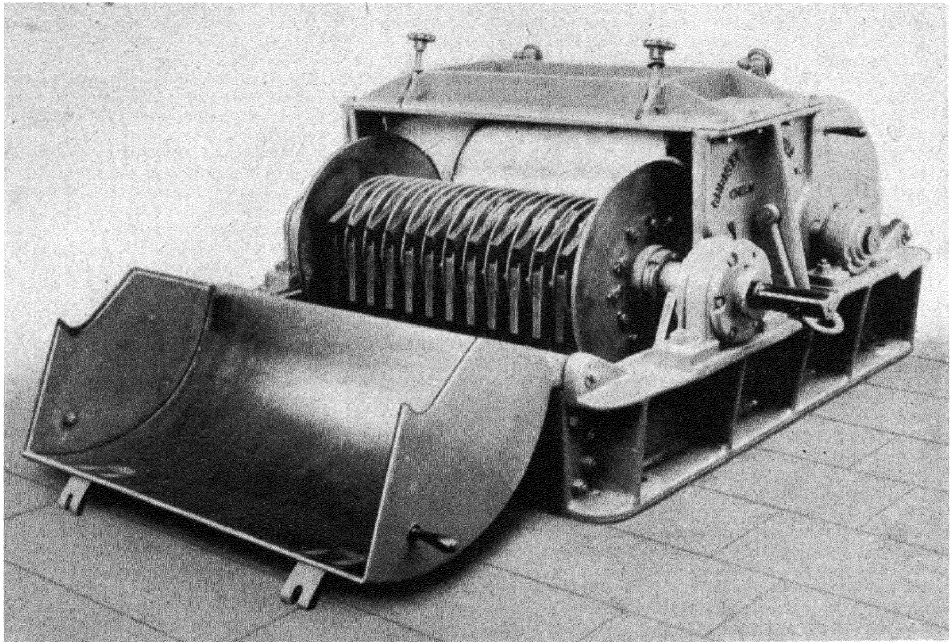


FIG. 80.—CHRISTY & NORRIS DOUBLE ROTOR MACHINE FOR SUPERPHOSPHATE

CHAPTER XII

COMPOUND MANURES AND MIXING SYSTEMS

THE preparation of compound manures to meet certain specific requirements is an important branch of the fertiliser industry. It is one which calls for a wide knowledge of chemistry, physics, mechanics and commercial economics.

Since 1926 there has been a demand for compound fertilisers which are capable of being applied to the soil by means of drills. Drillability cannot be attained, or at least is very unsatisfactory, with a mixture of fertilisers consisting of materials of different physical characteristics and various particle sizes. Powders are usually dusty when dry, and sticky when damp, and it is clear that crystalline or granular particles of predetermined size flow more readily than powders. The ability to apply a fertiliser by means of a drill is represented by its ease for uniform and regular distribution. If distribution is irregular, as necessarily occurred with machinery in use ten or twenty years ago, the quantity applied to the soil in proximity to the seeds may be sufficient to delay germination, or indeed to prevent it altogether, while the soil in proximity to other seeds may be insufficiently fertilised for best results, or conceivably may be deprived of any fertiliser. The response of a crop to the application of a fertiliser depends to a large extent on (a) its physical condition, (b) its chemical composition, and (c) its method of application.

It is partly a recognition of the foregoing fundamental considerations which has led to the manufacture of compound fertilisers in granular form in this country and on the Continent. But an equally important reason, which has already been referred to in Chapter I, is the desire to avoid insolubility and reversion of the superphosphate within the soil, and thus obtain a greater efficiency of use. The practical pioneers in this aspect of fertiliser manufacture are Messrs. Fisons, Ltd., and we are privileged in this book to give a view, illustrative of the drillability of granular fertiliser, and some photographs of various other granulating plants in Great Britain. In a brochure which has been circulated to the trade it is remarked that their further development is a factory designed to produce 50,000 tons per year of high-grade compound fertilisers *in a granular form*. These granular fertilisers contain water-soluble phosphate in the form of superphosphate, thus supplying such essential plant foods as sulphur, magnesium, and iron. Each granule is said to contain a proportion of plant foods, and being dust-free they readily flow—that is, they are easily drillable.

A range of ten complete fertilisers in a granular form is manufactured, and in addition one or two entirely new fertilisers are fabricated. Particulars of the new range of fertilisers and their analyses are given in Table 27, and one finds in Table 28 details of the various crops for which they are said to be peculiarly suitable, having regard to the different characteristics of the soil. It is emphasised that the new range offers a choice of a properly balanced fertiliser for all crops on all soils under normal circumstances.

The Amsterdamsche Superfosfaatfabriek, Utrecht, in a brochure, remark that “Asef” fertilisers are free from dust and homogeneous; that is, in each granule are the three elements of plant food, in the proper proportions. “Asef” fertilisers are made in different grades to meet varying requirements of plant food, and the particular soil to which they are applied. The usual types manufactured are as follows:—

12 × 10 × 18	10 × 24 × 24
17 × 15 × 18	4 × 20 × 30
10 × 12 × 16	12 × 16 × 20
6 × 18 × 30	8 × 20 × 25
9 × 16 × 21	13½ × 25 × 16

In these formulæ the first figure represents the percentage of nitrogen, the second the percentage of phosphoric acid, and the third the percentage of potash. In most types the nitrogen is present

in the form of ammonia, but in some types part of the nitrogen is supplied in the quick-acting nitrate form. The mixtures 17×15×18 and 12×16×20 are types in which nitrogen is supplied partly in the nitrate form and are particularly suitable for top dressing.

It was felt desirable to preface this chapter with details of the latest development before proceeding to deal with many aspects of a fundamental character. What follows relates to hitherto-established practice, which is of considerable significance to-day; but time may witness a supersession of this. A comprehensive list of compound and complete fertilisers, as supplied by an important artificial fertiliser firm some time ago, is given in Table 29, and is interesting from a chemical viewpoint as applying to the presumed requirements of certain crops.

The field experiments which have been conducted at Rothamsted may be assumed to afford data from which conclusions can be drawn as to the value of certain fertilisers for certain crops. But consideration reveals that the object of these experiments was mainly to demonstrate the action of the fertiliser rather than the requirements of the plant.

With the advance of knowledge, both as to the value of the fertiliser and the specific requirements of the soil, having regard to the question of the rotation of crops, it becomes increasingly

TABLE 27
Analyses of Granular F.P.P. Fertilisers

Name of fertiliser.	ANALYSIS.			
	Ammonia. Per cent.	Phosphates.*		Potash. Per cent.
		Water-soluble. Per cent.	Insoluble. Per cent.	
1. Supreme	3	23.5	4	6
2. Extra quality	3.5	21	3	3
3. C.A.P. (n)	8	20	1.5	2
4. P.E.P. (n)	5	18	1.25	10
5. Gold medal (n)	5	17.5	1.25	5
6. Universal (n)	7.5	16	9	5
7. Champion	6	15	3	6 (s)
8. 12 per cent potassic	6	15	6	12 (s)
9. Challenge	7.5	14	3	7.5
10. Bumper	10	14	4	5

* The water-soluble phosphates added to the insoluble phosphates gives the total phosphates.

(n) Partly nitric nitrogen.

(s) Sulphate of potash.

Three F.P.P. concentrated fertilisers in a granular form are manufactured to meet the requirements of farmers who desire fertilisers of this type:—

Standard.

20 per cent water-soluble phosphoric acid	43.66 per cent phosphates.
10 „ nitrogen	12.14 „ ammonia.
14 „ potash (sulphate and muriate).	

Light Land.

16 per cent water-soluble phosphoric acid	34.96 per cent phosphates.
7 „ nitrogen	8.50 „ ammonia.
15 „ potash (all sulphate).	

TABLE 28

Recommendations for Granular F.P.P. Fertilisers

Crop.	Class of soil.			
	Light.	Medium.	Heavy.	Black ten.
Barley	1	2 or 5	2 or 5	1
Beans and peas	1	1	1	1
Cabbages	6 or 10	3 or 6	3 or 10	6
Cauliflowers	6 or 10	6 or 9	5 or 9	4
Carrots	1 or 4	1 or 4	1 or 4	1
Celery	—	—	—	4, 8 or 9
Chicory	4	1	1	1
Fruit, Pears or plums	7	5 or 7	6 or 7	—
Apples	4 or 8	4 or 8	4 or 8	4 or 8
Raspberries	4	5 or 7	7 or 9	—
Gooseberries				
Black currants				
Grass, Spring	3 or 6	3 or 6	3 or 6	1
Summer	6	6	6	1
Hops	4	5 or 6	5 or 9	—
Kale	6 or 10	3 or 6	3 or 10	6
Kohl rabi	1	2 or 5	2 or 5	1
Linseed (seed or fibre)	4	1 or 2	1 or 5	1
Lucerne	1	1	1	1
Mangolds	5 or 9	5 or 9	5 or 9	5 or 9
Mustard	1	2	2 or 5	1
Oats	5	2 or 5	2 or 5	1 or 2
Potatoes, Earlies	6, 7 or 10	6, 7 or 10	6, 7 or 10	6, 7 or 10
Main	4 or 8	4, 6, 7, 8 or 9	6, 7 or 9	5, 6, 7 or 9
Rye	5	2 or 5	2 or 5	1 or 2
Sainfoin	1	1	1	1
Sugar beet	1 or 4	4, 6 or 9	6, 9 or 10	1 or 4
Swedes and turnips	1	2	2	1
Vetches	1	—	—	1
Wheat, Autumn	1	2	2	1
Spring	5	2 or 3	2 or 3	1 or 2
Market garden	4 or 8	6, 7 or 9	6, 7, 9 or 10	4, 6 or 8

During the war period, 1939-1945, the tendency has been towards reducing the number of grades. Only three or four grades have been prepared and these, generally have met the farmers' needs.

General.

20 per cent water-soluble phosphoric acid	43.66 per cent phosphates.
6 „ nitrogen	7.28 „ ammonia.
6 „ potash (all sulphate).	

All these granular fertilisers are packed in 1-cwt. bags.

evident that what would be ideal would be the preparation of compound manures having such a chemical composition as would meet the specific requirements of the soil and the conditions of farming, and would be of real economic merit.

It cannot be doubted that in the past the practice of applying a kind of average fertiliser has proved wasteful.

It is unnecessary here to enlarge further on this aspect. To the discerning mind it will be obvious that an important question arises. Briefly stated, it is this: is it better for the farmer to dictate the constitution of the compound manures which he shall apply, having regard to his peculiar knowledge of his own soil and conditions of farming, or should the fertiliser manufacturer continue to prepare average manures as in the past, with little or no regard to the nature of the soil and the farming conditions?

TABLE 29

	Calcium phosphate [Ca ₃ (PO ₄) ₂]		Nitrogen.			Potash.	
	Total.	Soluble.	N ₂ .	NH ₃ .	(NH ₄) ₂ SO ₄ .	K ₂ O.	K ₂ SO ₄ .
Gold medal barley	22	18	3.32	4.00	15.54	0.75	1.40
Special barley	27	20	2.05	2.50	7.66	0.50	0.92
Oat	25	19	2.05	2.50	9.66	1.25	2.34
Gold medal mangold	20	18	2.90	3.50	13.66	2.50	4.55
Special mangold	26	19	2.05	2.50	9.66	1.25	2.34
Pea and bean	28	15	2.90	3.50	13.66	3.00	5.85
Clover and grass	20	20	1.02	1.25	9.66	0.50	0.92
Extra special potato	16	14	4.55	5.50	21.34	8.00	14.80
Challenge potato	28	15	2.90	3.50	13.66	3.00	5.55
Special potato	17	16	1.65	2.00	7.77	3.00	5.55
Ammonium phosphate	22	20	4.12	5.00	19.43	—	—
Autumn wheat	28	20	1.25	1.50	5.87	—	—
Pure dissolved bones	35	18	2.45	3.00	11.68	—	—
Special dissolved bones	36	16	1.65	2.00	7.77	—	—
Bone compounds	28	20	1.25	1.50	5.89	—	—
" "	28	20	0.82	1.00	3.86	—	—
Calcium superphosphate		26	and upward		—	—	—
Lime superphosphate	35	28	0.42	0.50	1.98	—	—
" "	28	20	0.82	1.00	3.86	—	—
Special superphosphate	28	15	0.60	0.75	2.91	—	—
Potash superphosphate	35	23	—	—	—	5.00	9.25
Potassic supers	26	23	—	—	—	4.00	7.40
Basic potassic supers	25	23	—	—	—	3.00	5.55
Nitrate and phosphate top dressing	20	10	4.94	6.00	23.25	—	—
All-round garden fertiliser	28	8	—	7.00	—	6.00	—
Soluble garden fertiliser	—	20	—	7.00	—	7.00	—
Special garden fertiliser	14	14	—	3.50	—	3.00	—

That opinion will be divided on this question is clear. But it cannot be doubted that pending the time when the farmer appreciates scientific manurial principles it will be better for a system of collaboration to exist between the farmer and the fertiliser manufacturer. Such an arrangement would doubtless prove of mutual advantage.

It is not suggested that there is not collaboration at the moment; it is not suggested that

there are not farmers who have an admirable appreciation of the science of manuring. What is implied is that neither collaboration nor scientific farming has reached finality, and that there is opportunity for progress in the direction indicated.

Attempts to form a judgment of what is required by an account of what is removed from the soil year by year by the crops or animals raised on the farm are not too helpful. Under present conditions, perhaps under even the conceived ideal conditions to which reference has been made, the proper course of action in the matter of farming may resolve itself into "a judicious compromise adapted to all the various conditions of climate, soil, and markets."¹

A few words will be not inappropriate concerning the list of compound fertilisers given on p. 127. On the subject of preparing for a crop of barley of high quality, Hall points out, among other things, that phosphoric acid is a very essential constituent of any barley fertiliser, and, irrespective of tilth, it is desirable to give these crops 3 cwt. per acre of superphosphate, or its equivalent in steamed bone flour or phosphoric guano, on light soils poor in carbonate of lime.

As regards potash manures, Hall says that these must be carefully used and are only calculated to be valuable on light sandy or gravelly soil. He thus concludes that the following mixture is satisfactory for a barley manure, when barley follows one or more white straw crops and the land is no longer in high condition :—

- Ammonium sulphate, 0.5 to 1.5 cwt. per acre.
- Superphosphate, 3 cwt. per acre, or
- Steamed bone flour, 2 cwt. per acre.
- Sulphate of potash, 0.5 cwt. per acre, on light soils.

Contrast the above with the two barley manures of which details are given in the foregoing list. The following table gives information admitting of a comparison :—

TABLE 30
Hall's Basis of a Barley Manure, as discussed

Constituents.	Quantities per acre (say). cwt.	Quantities per ton of 20 cwt.	Per cent nitrogen, $\text{Ca}_3(\text{PO}_4)_2$ and K_2O respectively.	Units of nitrogen, $\text{Ca}_3(\text{PO}_4)_2$ and K_2O respectively.	Percentage N_2 and $\text{Ca}_3(\text{PO}_4)_2$ and K_2O respectively.
Sulphate of ammonia . . .	1	4.4	20.5	8.91	4.46
Calcium superphosphate . . .	3	13.3	30.0	3.99	19.95
Sulphate of potash . . .	0.5	2.3	49.0	0.113	0.56
		20.0			

The figures representing the percentages of the essential elements in the two compound barley manures are as follows :—

TABLE 31

Constituents.	"A" Quality.	"B" Quality.
	Per cent	Per cent
$\text{Ca}_3(\text{PO}_4)_2$ soluble	18.0	20.0
Total	22.0	27.0
N_2	3.32	2.0
K_2O	0.75	0.5

¹ A. D. Hall, *Fertilisers and Manures*, p. 306.

From an examination of the two foregoing tables it is clear that with the gold medal barley "A" in question slightly more sulphate of potash is used and a little less sulphate of ammonia and calcium superphosphate are employed. But substantially the mixture approaches that recommended by Hall. In the case of the special barley compound manure "B," it would appear from the wide difference in water-soluble calcium phosphate content that bone superphosphate is used in lieu of mineral superphosphate.

Take a compound manure for potatoes. Hall says it is more difficult to lay down general rules for the manuring of the potato crop, on account of the variety of tilths on which potatoes are grown and the differences in the yields aimed at. After dealing in detail with this aspect Hall suggests that the mixture of artificials should either be sown broadcast before the land is ridged up, or sown upon the farmyard manure in drills before the ridges are split.

He further states that for ordinary cropping, a mixture of 4 cwt. per acre of superphosphate, 1 cwt. of sulphate of potash, and 1 cwt. of sulphate of ammonia should be employed. When extra heavy crops are aimed at it is suggested that 2 cwt. or so of good guano may be added to the mixture specified, and a further 1 cwt. of sulphate of ammonia may be applied as a top dressing when the haulm is beginning to appear. Let us examine now the mixture recommended by Hall for a normal potato crop. Its characteristics are set out in Table 25.

If reference is now made to Table 29 it will be seen that Table 32 more nearly resembles the extra special potato manure than anything else. In any case, it is obvious that there is a large amount of latitude in the composition of compound manures, and that this latitude is dictated by local circumstances and special conditions applying to crop rotation and the nature of the soil, etc. It will be appreciated that it is no part of our task to attempt to reconcile the mixtures suggested by important fertiliser manufacturers with those recommended by such experts as A. D. Hall, F.R.S., late Director of the Rothamsted Experimental Station.

TABLE 32

Constituents.	Quantities per acre (say).	Quantities per ton of 20 cwt.	Per cent. nitrogen, $\text{Ca}_3(\text{PO}_4)_2$ and K_2O respectively.	Units of nitrogen, $\text{Ca}_3(\text{PO}_4)_2$ and K_2O respectively.	Percentage N_2 and $\text{Ca}_3(\text{PO}_4)_2$ and K_2O respectively.
	cwt.				
Sulphate of ammonia	1	3.4	20.5	0.697	3.9
Calcium superphosphate	4	13.2	30.0	3.960	19.8
Sulphate of potash	1	3.4	48.8	1.660	8.3
		20.0			

Reference to this aspect has been made, and comparisons have been instituted, because it was believed that the matter would be of general interest as a preliminary step to the treatment of the subject of compounding from the chemical point of view. Some compound manures are at times prepared from scrap and refuse materials that are unsuitable for direct use. Such materials usually undergo chemical and mechanical treatment in order to render them more assimilable by the plants. Leather cuttings, waste, shoddy, and other such materials are used, and after treatment they serve as ingredients for compound manures.

In other cases, such as those which have already been the subject of discussion, simple fertilisers, which do not react on each other, are mixed in various proportions. There is no chemical combination (or if any, it is somewhat obscure), but merely a mechanical mixture of certain constituents, to give a "compounded" manure to suit special crops.

It is the practice of British fertiliser manufacturers to work in hundredweights to the ton. To determine the percentage of the constituent elements—water-soluble $\text{Ca}_3(\text{PO}_4)_2$, N_2 , and K_2O in the ultimate mixture—it is merely necessary to multiply the weights in which the simple

fertilisers are compounded by the figure representing the percentage of the constituent elements which each ingredient contains, and subsequently to multiply by five. This will give the units of the constituent elements which the compound fertiliser contains. Thus :

- (a) 8.75 cwt. of sulphate of ammonia— $20.5 \text{ per cent } N_2 \times 5 =$
 (b) 11.25 cwt. of calcium superphosphate— $35.0 \text{ per cent } N_2 \times 5 =$

 20.00 cwt.

$$(a) 8.75 \times 20.5 \times 5 \div 100 = 8.95 \text{ per cent } N_2.$$

$$(b) 11.25 \times 35.0 \times 5 \div 100 = 19.68 \text{ per cent } Ca_3(PO_4)_2.$$

If the P_2O_5 unit figure is desired, then the $Ca_3(PO_4)_2$ figure must be divided by 2.185, thus :

$$19.68 \div 2.185 = 9.00 \text{ per cent } P_2O_5.$$

From the foregoing figures it is clear that to make a mixture containing 1 per cent of nitrogen, 19 cwt. of superphosphate, and 1 cwt. of sulphate of ammonia should be used. A mixture containing (say) 6 per cent of nitrogen can be made by using 14 cwt. of calcium superphosphate and 6 cwt. of sulphate of ammonia. Such mixtures are used occasionally for special purposes.

Detailed consideration will be given later to the best methods of mixing from the mechanical point of view. For the moment it is expedient to confine attention to matters of a chemical character. It is known that sulphate of ammonia retards the reversion of calcium superphosphate. Sulphate of ammonia, when admixed with calcium superphosphate, shows a distinct tendency to cake, nay, indeed, a definite "set" almost invariably takes place.

It is true that this setting invariably takes place slowly. That it causes inconvenience cannot be doubted. Not infrequently the bags arrive at the farm from the manufacturer's warehouse in an unfit condition for distribution on the land. Evidences of distinct cementing are revealed by the hard character of the compound fertiliser. At times it is necessary to cut the bags away. Wherever the fertiliser manufacturer has room and can manufacture ahead, the difficulty in question can be overcome. What is necessary is to mix the compound manure (that is, the ammoniated superphosphate) and store it until the fertiliser has completed its cementing propensity. Afterwards it should be reground and screened, so as to ensure a satisfactory condition.

Many experiments have been conducted, not only to determine the conditions under which the setting in question is most prolific, but also to ascertain if setting can be obviated by using a better quality of sulphate of ammonia, namely, the neutral and dry variety.

The results of these experiments have elicited the fact that mixtures containing about 5 to 6 per cent of ammonia give the greatest trouble. The use of the neutral, dry quality of sulphate of ammonia does not arrest the setting, and although it may possess advantages for the purpose in question which the acid-containing salt does not possess, it cannot be said that setting is obviated.

It is known that setting of ammoniated superphosphate can be prevented, but only at the expense of producing a moist, sticky product. What has to be decided in this connection is this : is it better to attempt to obviate setting, or to hasten setting, and then rectify the condition afterwards ?

Many have reached the conclusion that the last-named course is the better. Of course, something more than regrinding is necessary. The material must be passed through a fine sieve, so as to ensure something approaching a uniform size, free from lumps. Lumps, even if present to a small extent, will militate against the use of such a product by means of drills.

At most large works in this country, when a mixture of calcium superphosphate, sulphate of ammonia, and sulphate of potash is required, it is batched and allowed to set in the heap, pending delivery. A precaution which is usually taken is to ensure that the compound manure in question is filled into a bag large enough to hold a predetermined amount comfortably, so that there is freedom for the mixture to move about in transit. This is usually found to be effective in obviating any further setting. Occasionally, as an additional precaution, a little finely ground bone flour is introduced.

It is known that the formation of a double compound of calcium sulphate and ammonium sulphate results when superphosphate and neutral, dry sulphate of ammonia are mixed intimately and stored. Particularly does this action develop when the superphosphate is slightly damp. Where the admixture of ammonium sulphate with calcium superphosphate is likely to give a higher

unit value in the ultimate product than that required or than that for which there is a demand, it is usual to add a certain amount of gypsum, or insoluble phosphate, to reduce the percentage of soluble phosphate in the compound manure.

For example, 13 cwt. of calcium superphosphate having a content of 30 per cent water-soluble calcium phosphate, when mixed with 7 cwt. of ammonium sulphate, will give a compound manure having 20 per cent water-soluble calcium phosphate and 7 per cent of nitrogen.

TABLE 33

	cwt.	Per cent.	
Calcium superphosphate	13	30	19.5% soluble calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$.
Sulphate of ammonia	7	20.5	7.0% nitrogen, (N_2).

But the above compound fertiliser may be too concentrated in point of water-soluble calcium phosphate content, and to reduce this to the limit for which there is a demand, it is necessary to reduce the water-soluble calcium phosphate content by the addition of gypsum or insoluble phosphate. It is an advantage to use mineral phosphate for such a purpose, although such a mineral phosphate must be used as causes the least possible reversion.

An interesting article bearing indirectly on this aspect, contributed by Robertson,¹ is well worth examination at this juncture.

The "Parrish" process² for the production of ammoniated fertilisers containing relatively high proportions of monocalcium phosphate is one of importance, in view of the developments in the matter of the production of granular compound fertilisers. This process provides for the use of concentrated gas liquor containing 12 to 20 per cent of ammonia by weight, being neutralised with sulphuric acid, and the resultant magma, containing 40 per cent of ammonium sulphate, being evaporated in a vacuum evaporator until a magma containing 0.1 to as much as 45 per cent sulphuric acid (added sulphuric acid) is obtained. The latter magma, with a maximum percentage of free acid, can be used to treat ground phosphate rock in the production of an excellent three-element fertiliser, because sulphate of potash can be added during the mixing of the acid magma with phosphate rock. Thus the best conditions obtain for granulation, as the free phosphoric acid can be distributed throughout the mass, subsequently passed to a suitable mixer and dried and granulated.

By varying the free acid content of the ammonium sulphate magma, varying ranges of P_2O_5 , N_2 , and K_2O (this involves addition of sulphate of potash or potash salts) can be obtained. The feature of the process is the obviously inexpensive method of deriving the nitrogenous matter, in the form of ammonium sulphate, distributed throughout the mass of the three-element fertiliser.

Potassic Superphosphate

To appreciate the use of potassium fertilisers in the ordinary routine of farming, one must inquire into the part played by potash in the nutrition of plants or crops.

Water-culture experiments demonstrate that it is an indispensable element. But this is not the only evidence of the undoubted utility of potassium. It plays an essential part in the mechanism of the process of assimilation.

Where there is an absence or deficiency of potassium, the manufacture of carbohydrates, like starch, sugar, and cellulose, is retarded. In point of fact, it is crops which are rich in carbohydrate which require, indeed, which are dependent upon, an adequate supply of potash.

The effect of potash upon mangold crops has been strikingly demonstrated by experiments conducted at Rothamsted during the twelve years 1895 to 1906. In these trials it was shown that

¹ "The Rate of Reversion of Mixtures of Superphosphate with Basic Slag and Rock Phosphates," *J.S.C.I.*, 1917, p. 626.

² *B.P.* 445,029.

“ potash increased the crop in every case, except where nitrate of soda had been used as the nitrogenous cross dressing, in which case the soda liberates so much potash from the soil that specific application of potassic manures is unnecessary.”

Another feature which potash displays is its value in promoting the growth of clover and all leguminous crops. Here potash aids assimilation.

Coming now to the question which immediately concerns us—the production of compound fertilisers— it can be said that potash salts, such as the chloride or sulphate, are almost invariably used. Rarely are low-grade potash salts, such as blast furnace or cement kiln dust, employed, as they are too low in potash content to be of much value. Similarly, wood ashes contain little potash, and the high content of carbonate renders them, for the most part, objectionable. Where chloride of potash is used in the production of a compound fertiliser, it will invariably be found that the mixture becomes deliquescent on long exposure. Generally the potassium manures have a tendency to dry the superphosphate and to obviate reversion.

The more usual potash fertilisers are kainit, muriate of potash, and sulphate of potash. All potash manures should be valued according to their potash (K_2O) content.

In the cases of muriate of potash and sulphate of potash, the percentages of potassium chloride (KCl) and potassium sulphate (K_2SO_4) respectively are sometimes quoted. It is important that invoices should state the percentage of potash (K_2O). Below will be found a table setting out the percentage of K_2O , the current prices (1938), and the unit prices.

TABLE 34

	Potash (K_2O).	Price per ton, c.i.f., London.	Unit price.
	Per cent	£ s	(say) £ s.
Kainit	14	2 15	4 0
Potash salts	30	5 1	3 4.4
Muriate of potash, 80 per cent KCl	50	8 8	3 4.7
Sulphate of potash, 90 per cent K_2SO_4	48	10 0	4 2

It will be appreciated that in deciding on the form of potash to use, the important determining factor should be the price per unit, and the cost of transport.

The following grades of potash fertilisers are now available :

TABLE 35

Kainit	14 per cent K_2O .
Potash salts	20 " "
" " " " " "	30 " "
Muriate of potash	80 " $KCl=50$ per cent K_2O .
Sulphate of potash	90 " $K_2SO_4=49$ " "

A not uncommon procedure is to use a potash salt containing about 30 per cent of K_2O . One cwt. of such a salt, used in conjunction with 19 cwt. of superphosphate, gives a compound fertiliser containing 1.5 per cent of K_2O .

When 5 cwt. of potash salts and 15 cwt. of superphosphate are mixed, a compound fertiliser is obtained, having a content of 7.5 per cent of K_2O .

It is within such limits as the foregoing that fertiliser manufacturers generally work.

Potassic Basic Slag

Complete Manures

Apart from the difficulties which have been referred to when dealing with ammoniated superphosphate and potassium superphosphate, no peculiar problem arises in the production of compound manures.

Some years ago it was suggested by the Ministry of Agriculture and Fisheries that it would probably be more economical for the farmer to undertake his own mixing. While such an operation may fittingly occupy farm labourers at slack periods, it must be remembered that hand mixing is not nearly so efficient as mechanical mixing. Evidence of this will be given later. Further, it is feared that the mechanical condition of the complete compound fertilisers would suffer, and bad distribution would ensue.

On the whole, there are cogent reasons for leaving the work of compounding in the hands of the fertiliser manufacturers, provided there is suitable collaboration which will admit of the most satisfactory complete fertiliser being produced for the specific requirements of the soil and the conditions of farming.

A few words concerning the fertilisers which may or may not be mixed will not be out of place at this juncture.

Sulphate of ammonia, or other ammoniacal fertiliser, must not be mixed with any fertiliser containing free lime, such as basic slag or basic superphosphate, nor should it be mixed with precipitated phosphates, nor with fertilisers containing much calcium carbonate, such as Belgian or Algerian phosphates.

If such a practice is pursued, it will be found that free ammonia is generated, and its presence will soon be recognised by its characteristic pungent smell.

Sulphate of ammonia may be mixed with calcium superphosphate, bone manures, fish meal, nitrate of soda, salt, and most forms of potash. With mixtures of sulphate of ammonia and superphosphate we have already dealt, as indeed with mixtures of the two foregoing fertilisers with potash salts. Reference has already been made to the moist and pasty condition which potassium superphosphate, or a compound fertiliser of ammonium sulphate, superphosphate, and potash, assumes, if not sown soon after being made.

One method of obviating this disability, and of improving the mechanical condition of the compound fertiliser, is to mix a dry medium such as bone flour, fine bone meal, or castor meal to the extent of about 10 per cent.

Nitrate of soda should not, under ordinary circumstances, be mixed with superphosphate or dissolved bones. Apart from a bad mechanical condition resulting, a loss of nitrogen will generally follow. The foregoing difficulty may be overcome by the addition of an appreciable proportion of drying manures, of which mention has been made. Nitrate of soda may be mixed with salt or any potash fertiliser without adverse result. It may be mixed with raw mineral phosphates, but the mixture should be used at once, and not be stored.

Nitrolim may be used in conjunction with basic slag, bones, or any potash fertiliser, and it may also be mixed with good, dry samples of superphosphate. In this case, however, a little heat may be developed, and it is conceivable that part of the water-soluble phosphate may be reverted. Nitrate of lime is not suitable for the production of compound manures.

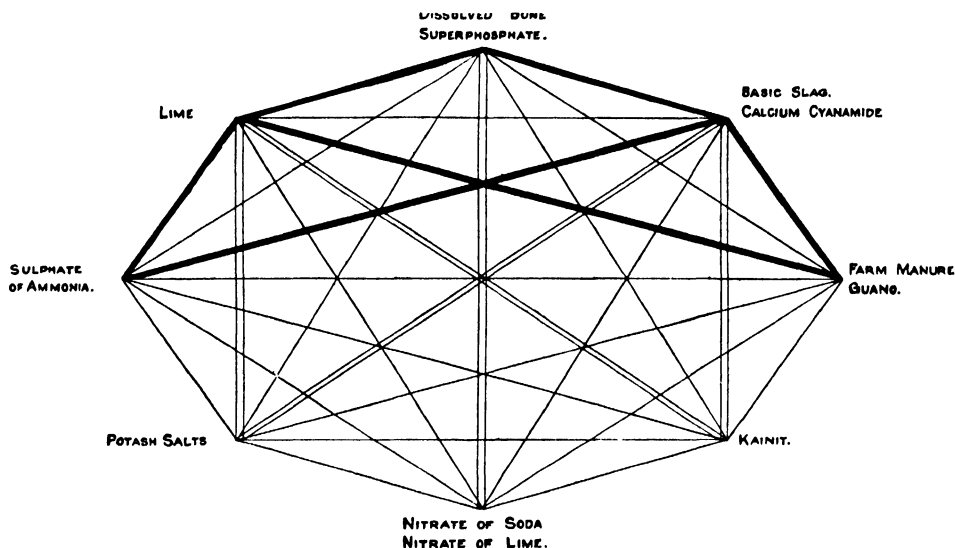
Superphosphate should not, under ordinary circumstances, be mixed with basic slag, precipitated phosphate, or ground mineral phosphate (except under predetermined conditions), otherwise the water-soluble phosphate of the superphosphate will be converted to the water-insoluble form, dependent on the extent of the available lime.

Bone flour and bone meal are immune from such action, unless the mixture is stored for an appreciable time. The addition of basic slag to superphosphate and bone manures containing superphosphate has been referred to, and the conditions under which its incorporation may take place have been cited. Steamed bone flour is preferred to basic slag in many cases by most fertiliser manufacturers.

Where several constituents are mixed, the advantages of various forms and degrees of solubility can readily be obtained. It should be mentioned here that rape dust is used for avoiding the "setting" in compound manures.

Some complete fertilisers which are used contain as many as eight to ten constituents. Blood is a friable product, and is used to give a high nitrogen content and the necessary physical characteristics for a complete vine fertiliser.

On the subject of the fertilisers that may be mixed and may not be mixed, apart from the foregoing observations, it is suggested that the diagram of Dr. Geeken (Fig. 81) should be carefully examined. Indeed, it will well repay careful study.



In this diagram, fertilisers joined by a *thick line* should *not* be mixed together at any time, although they may both be applied to the same land. Manures joined by a *double thin line* may be mixed together *shortly before application*. Manures joined by a *single line* may be mixed together *without any precautions*.

FIG. 81.—DR. GEEKEN'S DIAGRAM OF COMPOUND MANURES

Some complete compound fertilisers recommended by the Ministry of Agriculture and Fisheries may be given, for purposes of comparison with those recommended by certain fertiliser manufacturers.

In this connection it must be remembered that it is impossible to guarantee that any particular mixture will be specially adapted to one or another crop under all conditions. It is for this reason that we have emphasised repeatedly the desirability for collaboration between the actual user and the fertiliser manufacturer, who is responsible for compounding such manures.

The following particulars of complete compound manures are adapted from average conditions.

The quantities stated should be sufficient for one acre under average conditions.

Wheat, Oats, Barley.—For application at seed-time, or early spring, for wheat to be sown after a corn crop, and in soil not yet manured.

Sulphate of ammonia.	$\frac{3}{4}$ cwt.	$=\frac{3}{4} \times 20 \times 4/13$	$= 4.6$ nitrogen
Superphosphate.	$1\frac{1}{2}$ „	$= 3/2 \times 30 \times 4/13$	$= 13.8$ soluble phosphate
Steamed bone flour.	$-\frac{1}{2}$ „	$= \frac{1}{2} \times 1 \times 4/13$	$= 0.1$ nitrogen
	$-\frac{1}{2}$ „	$= \frac{1}{2} \times 60 \times 4/13$	$= 9.2$ insoluble phosphate
Sulphate of potash.	$\frac{1}{2}$ „	$= \frac{1}{2} \times 49 \times 4/13$	$= 7.5$ potash

The percentage composition of the mixture is therefore 4.7 nitrogen, 13.8 soluble phosphate, 9.2 insoluble phosphate, 7.5 potash.

Mangolds.—For application at seed-time.

1½ cwt. sulphate of ammonia	} containing	nitrogen	5.7 per cent
2½ „ superphosphate		sol. phosphate	14.3 „
½ „ steamed bone flour		insol. phosphate	5.7 „
¼ „ sulphate of potash		potash	7.0 „

In addition, it is advisable to apply separately about 4 cwt. of common agricultural salt.

Swedes, Turnips.—For application at seed-time.

¾ cwt. sulphate of ammonia	} containing	nitrogen	3.0 per cent
3 „ superphosphate		sol. phosphate	17.1 „
1 „ steamed bone flour		insol. phosphate	11.4 „
½ „ sulphate of potash		potash	4.7 „

Potatoes, Carrots.—For application at planting and seed-time.

1½ cwt. sulphate of ammonia	} containing	nitrogen	3.9 per cent
3½ „ superphosphate		sol. phosphate	16.2 „
¾ „ steamed bone flour		insol. phosphate	7.0 „
1 „ sulphate of potash		potash	7.5 „

Beans, Peas, Lucerne, Sainfoin.—For application at seed-time for beans and peas, and as a spring top-dressing for lucerne and sainfoin.

½ cwt. sulphate of ammonia	} containing	nitrogen	2.0 per cent
3½ „ superphosphate		sol. phosphate	19.1 „
1 „ steamed bone flour		insol. phosphate	10.9 „
½ „ sulphate of potash		potash	4.5 „

“Seed” Hay.—As for oats. For application in early spring.

Meadow Hay.—For application in early spring.

1 cwt. sulphate of ammonia	} containing	nitrogen	4.5 per cent
2½ „ superphosphate		sol. phosphate	16.7 „
½ „ steamed bone flour		insol. phosphate	6.7 „
½ „ sulphate of potash		potash	5.4 „

The main object of introducing steamed bone flour into the mixture is that it may act as a “drier,” and thus facilitate distribution. Fine bone meal or castor meal might be used instead, with similar effect.

Having dealt with the chemical aspect relating to compound manures, it will be desirable now to regard the matter from what may be called the mechanical viewpoint.

There still exist diverse opinions among fertiliser manufacturers as to what constitutes a thorough mixing, or compounding, of manures, and it is surprising that in some works even to-day one still finds compounds undergoing manufacture by turning over the ingredients on the floor. Where this is done, there is a belief in the minds of those in control that the subsequent elevating and screening of the product thoroughly mixes the materials. Little evidence is required to prove that this is a delusion. Variations in the analytical results of tests taken from the same batch are surprising.

If the fertiliser materials were all of the same fineness and quite dry, and all of approximately the same density, there would be less chance of variation throughout the batch. However, this is far from being the case. Superphosphate is often slightly damp and does not easily blend with some of the ingredients used to compound with it.

The following table gives the approximate weights per cubic foot of some of the different fertiliser materials used. The figures are averages of results taken at different times at different plants, and are expressed in round numbers. The materials were not packed, but simply “shaken down.”

TABLE 36
Approximate Weights per Cubic Foot of several Fertiliser Materials

Materials.	Weight per cub. ft.
Superphosphate	55-60 lb., dependent on particle size and dryness.
Ground phosphate, 80%—100 mesh	75 lb.
Dried blood	30 lb.
Tankage	45 lb.
Cottonseed meal	45 lb.
Nitrate of soda	85 lb.
" Metro " sulphate of ammonia	54 lb.
Muriate of potash	59 lb.
Sulphate of potash	80 lb.
Kainit	85 lb.

As will be seen from this table, the densities of these materials vary considerably, as also their mechanical condition, so it is not difficult to understand why hand-mixing is not likely to give a homogeneous product.

Where hand-mixing is employed, the procedure is carried out somewhat on the following lines :

One ton is usually the size of the batch. The various ingredients comprising the batch are spread out on the floor, one on top of the other, in front of an elevator. Three or four men standing round turn the heap over once or twice and then shovel it into the elevator hopper. The materials are elevated to a screen, and that which passes through the screen falls into a bagging hopper: the tailings drop down another chute into a disintegrator, and thence again to the elevator and up over the screen.

In such a process the personal factor counts a great deal in the uniform results obtained, but there is no reliable safeguard. The varying results obtained from some actual mixings are as follows :

TABLE 37

Formulated for.			Analysis taken.		
Available P_2O_5 .	Ammonia NH_3 .	Potash K_2O .	Available P_2O_5 .	Ammonia NH_3 .	Potash K_2O .
10	4	4	11.46	3.74	3.65
10	4	4	10.81	4.01	4.58
10	4	4	10.62	3.80	3.75
10	2	2	10.72	2.12	1.89
10	2	2	11.15	1.71	2.55
10	2	2	8.72	2.42	2.30

These results show conclusively that hand-mixing is quite unreliable, and yet this method is still used to-day by some fertiliser manufacturers, and regarded by them as representing good practice.

If this method of mixing is crude, it is better than is likely to be achieved by the farmer mixing the component materials on the barn floor. This system can only be superseded by demonstrating to the farmer that compound manures, as prepared in modern plants, are more economical than any home-mixed product. It is now an established fact that uniformly mixed and well-balanced fertilisers give more uniform crop production. When the farmer is convinced of this he will cease to do his own mixing and buy compounds which have been mixed in a scientific manner by up-to-date machinery.

The principle on which all modern mixing plants are designed is that only screened materials should go to the mixer. The charge is held in the mixer hopper until the tailings have passed through the pulveriser and are screened a second time, when they join the main portion of the batch in the mixer hopper. The whole batch, which is generally 1 ton, is then of an even grade and can be thoroughly mixed in a few minutes with the mixing action to which it is subjected.

As a proof of the accuracy of a modern mixing plant the following test, which is one of many, is convincing. The compound which was made gave a theoretical analysis (based on the analyses of the materials used) of :

8.77	per cent	available P_2O_5 .
2.04	„	ammonia, NH_3 .
2.20	„	potash, K_2O .

Ten samples of the finished goods taken at different times out of a 20-ton throughput gave the following results :

TABLE 38

Available P_2O_5 .	Ammonia NH_3 .	Potash K_2O .
8.79	1.98	2.23
8.75	1.96	2.22
8.61	1.98	1.96
9.18	2.20	2.29
8.74	2.01	2.25
8.78	2.10	2.11
8.72	2.08	2.18
8.69	2.08	2.29
9.08	2.10	2.09
8.67	2.01	2.14
Average 8.80	2.05	2.17

In the compounding of manures the Americans have led the way, and some of their mixing plants are of great interest.

The developments in the fertiliser industry in the United States have been along lines somewhat different from those followed in the European field. For instance, there are several large works which confine themselves solely to the manufacture of superphosphate, and these are designed on a very large scale. On the other hand, a large number of firms in the trade do not manufacture any superphosphate at all, but are engaged exclusively in the preparation of compound manures.

These dry-mixing plants are designed on the most up-to-date lines, and some of them are capable of producing 75,000 tons per annum. In some cases the building is approximately 70 to 80 feet span and 200 to 300 feet long, and is served by one or two overhead travelling cranes, as shown in Fig. 82. Approximately two-thirds of the building is used for the storage of superphosphate and other raw materials.

Fig. 83 shows the method employed at large works for storing the raw materials in separate bins. These bins are sub-divided by means of timbers laid horizontally with packing pieces between to allow an air space and are placed between rows of stanchions, as shown in the illustration.

The materials to be mixed are taken from the storage heaps and pens by means of the overhead crane and dumped into a series of storage bins, each holding approximately 20 tons. These bins may vary in number—nine are shown in Fig. 84. They are placed well above the floor, and underneath each one there is a weighing scale, which weighs off the correct amount of material to be drawn from the bin. Batches to be mixed generally total 1 ton, and each scale weighs a certain proportion of the batch. When each scale hopper contains the specified weight of its own raw material they are emptied on to a belt conveyor running underneath and along the length of the hoppers.

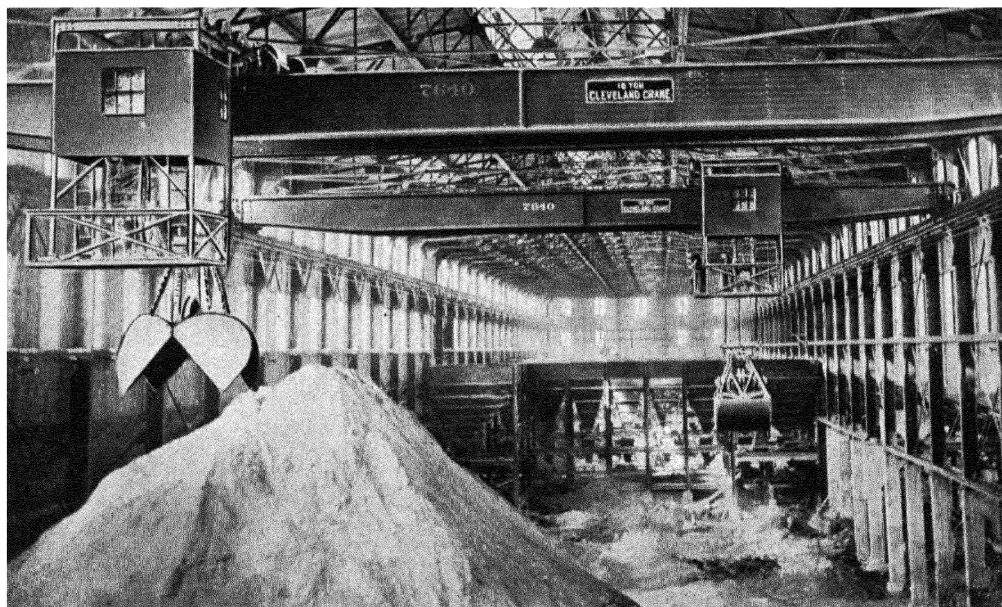


FIG. 82 --FERTILISER MIXING PLANT WITH OVERHEAD CRANE

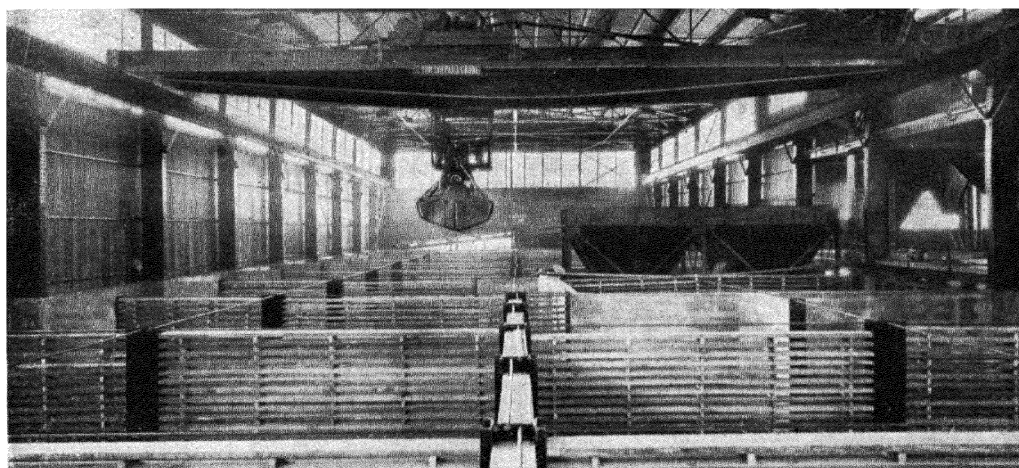


FIG. 83.--METHOD EMPLOYED AT LARGE WORKS FOR STORING RAW MATERIALS IN SEPARATE BINS.

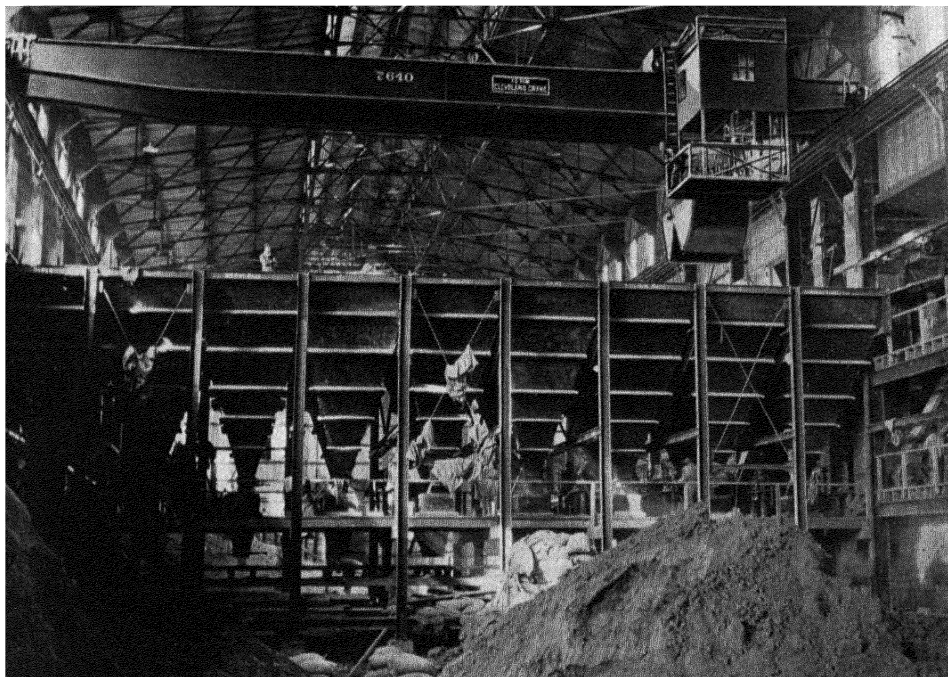


FIG. 84.—HOPPERS AND WEIGHERS PRECEDING FERTILISER MIXING PLANT

Fig. 85 shows a Sturtevant fertiliser mixing plant.

The conveyor belt "C" discharges into an elevator, which delivers the materials to a vibrating screen F. The tailings are delivered by a chute to a pulveriser H, and from there are elevated to the screen a second time, joining the main batch in the mixer hopper, before any material enters the mixer. The mixer inlet is then opened, and the batch, which has been properly disintegrated and screened, is introduced. The materials are only in the mixer a few minutes when the discharge gate is opened, and the mixed compound is delivered to a bagging hopper underneath, from which it is filled into bags. The bags are weighed and dropped on to a slat conveyor, which either delivers to railway wagons or electric trucks for taking to storage. The men who do the sewing ride on this conveyor with the bags, sewing as they move. When finished, they walk back, threading their needles on the way, and repeat the operation.

While the materials are being mixed and discharged from the mixer another batch is being collected in the mixer hopper, so that no interval of time elapses between the mixings. As soon as one batch is discharged from the mixer another is ready to be introduced.

When the plant is used as a basing unit the mixed goods are discharged from the mixer to a short belt conveyor L, which delivers to a pit N. It is removed from this pit by the crane bucket and stored where desired.

A plant such as that described will handle and mix 25 to 30 one-ton batches per hour. The power required for driving the mixing equipment is approximately 25 b.h.p.: this does not take into account the overhead crane.

The following men are required to operate the plant :

- One man on the crane.
- Three men on the weighers under storage hoppers.
- One man on the mixer.
- Two men weighing and sacking.
- Four men sewing.

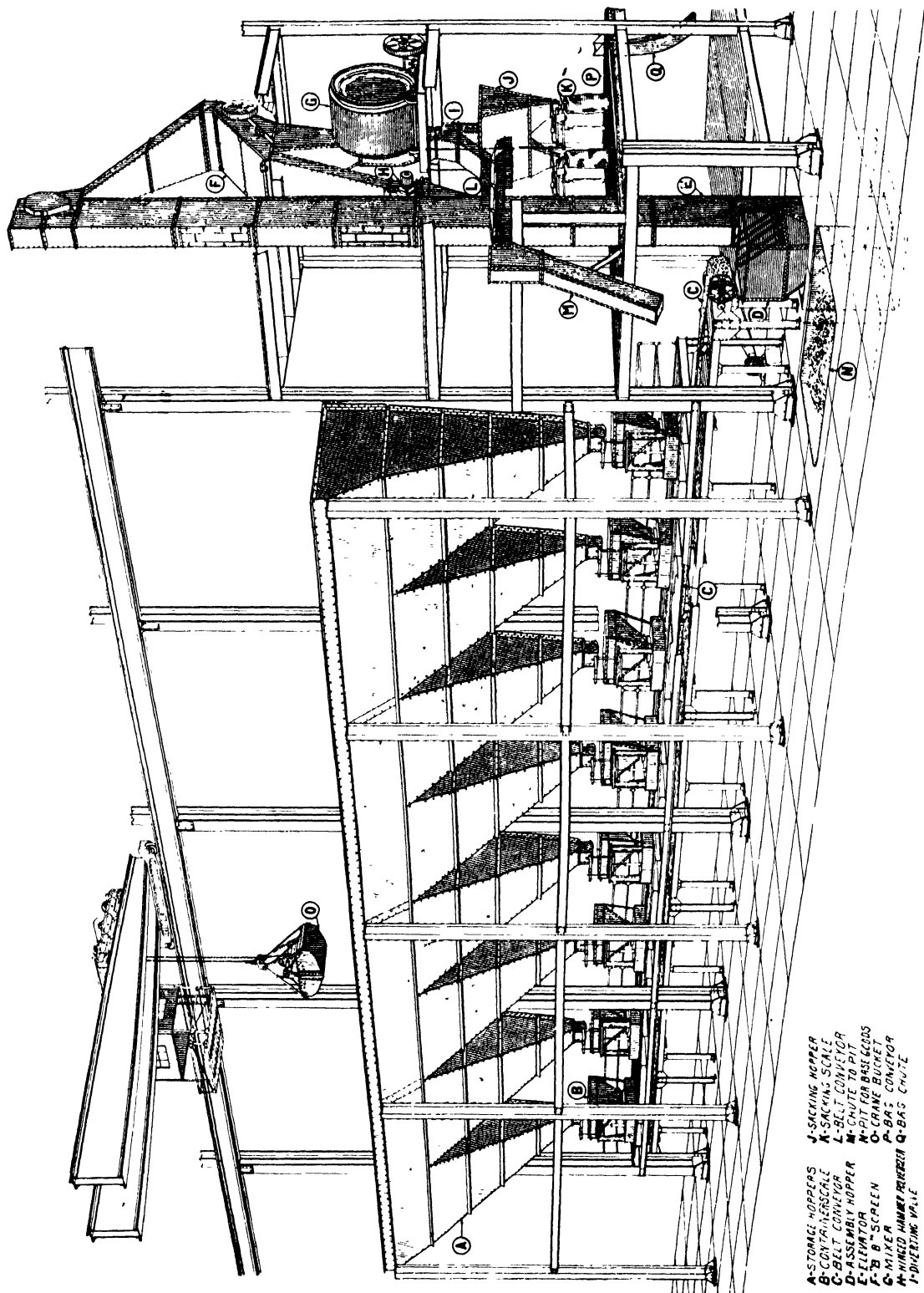


FIG. 85.—STURTEVANT FERTILISER MIXING PLANT

- A—STORAGE HOPPERS
- B—CONTRACTOR SCALE
- C—BELT CONVEYOR
- D—ASSEMBLY HOPPER
- E—ELEVATOR
- F—B—SCREEN
- G—MIXER
- H—MIXER
- I—MIXER
- J—SACKING HOPPER
- K—SACKING SCALE
- L—BELT CONVEYOR
- M—CHUTE TO PIT
- N—PIT FOR BASE GOODS
- O—CRANE BUCKET
- P—BAG CONVEYOR
- Q—BAG CHUTE
- R—PULVERISING PLATE

Referring to Fig. 85, it will be observed that the raw material hoppers are arranged along the side of the building parallel to the crane track. When these hoppers are placed across the building, or at right angles to the crane track, as in Fig. 84, a large storage space is wasted, representing in some cases approximately 2500 tons. When they are arranged as shown in Fig. 85 the hoppers do not interfere with the maximum storage capacity of the crane bay. They occupy what is open or waste space along the base of the pile, as the natural slope of the pile reaches only to the supporting columns.

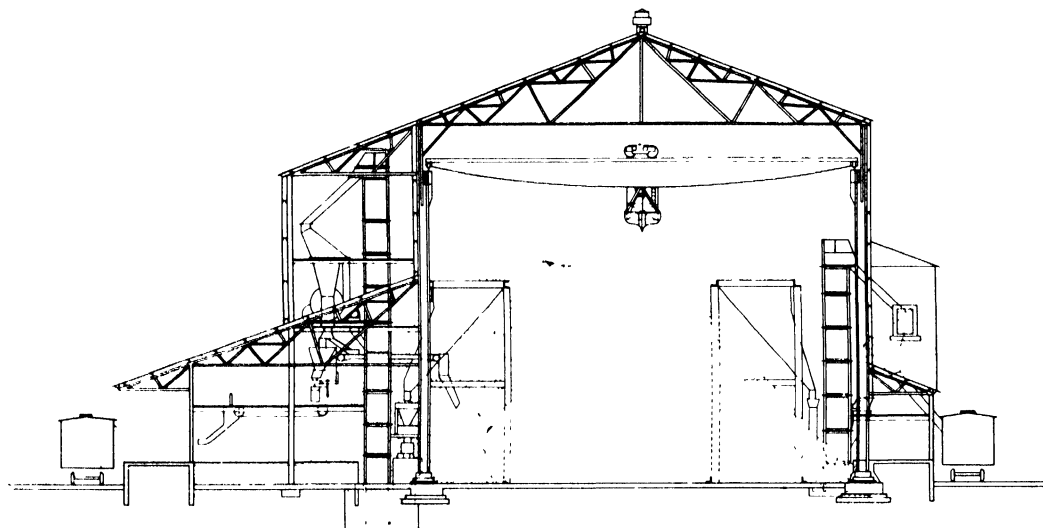


FIG. 86.—SECTION OF BUILDING SHOWING MIXING AND SHIPPING UNITS

Fig. 86 shows the section of a large modern superphosphate store, with the compounding plant arranged on the left and a bulk shipping unit, or dressing plant, arranged on the right. Neither of these plants interferes to any great extent with the storage space in the crane bay, and the facilities are such that large quantities of finished goods can be despatched daily.

Compound mixing plants on a smaller scale, but designed on the same principle, are operating in works of moderate dimensions on both sides of the Atlantic. When there is no overhead crane the plant is arranged as shown in Fig. 87. The raw materials, which have previously been weighed, are brought in hand-carts or barrows to a receiving hopper placed level with the floor. The various ingredients comprising the batch, which is usually 1 ton, are tipped into the hopper and elevated to a vibrating screen. There is a coarse grid over the hopper to retain any large lumps which might choke the elevator feed. These are broken with the tap of a shovel. That portion of the batch which is fine enough to pass the screen is collected in the mixer hopper; the hard cores or tailings are delivered to a hinged hammer pulveriser, thence to the elevator and again over the screen, when they join the main portion of the batch in the mixer hopper. The batch, which is now properly sized and disintegrated, is fed into the mixer, and after a minute or two the discharge gate of the mixer is opened and the mixed product is elevated to a bagging hopper, from which it is bagged and weighed. While the mixer is discharging, the next batch is being collected in the hopper, so that the mixer is working practically continuously.

When the plant is used for mixing "base goods" for storage, the second elevator discharges into the hopper at the higher level, from which trucks are loaded and run back into the store.

A Sturtevant 1-ton mixing unit, as shown in Fig. 87, will handle 10 to 15 tons per hour, dependent on the facilities for bringing the materials to the plant.

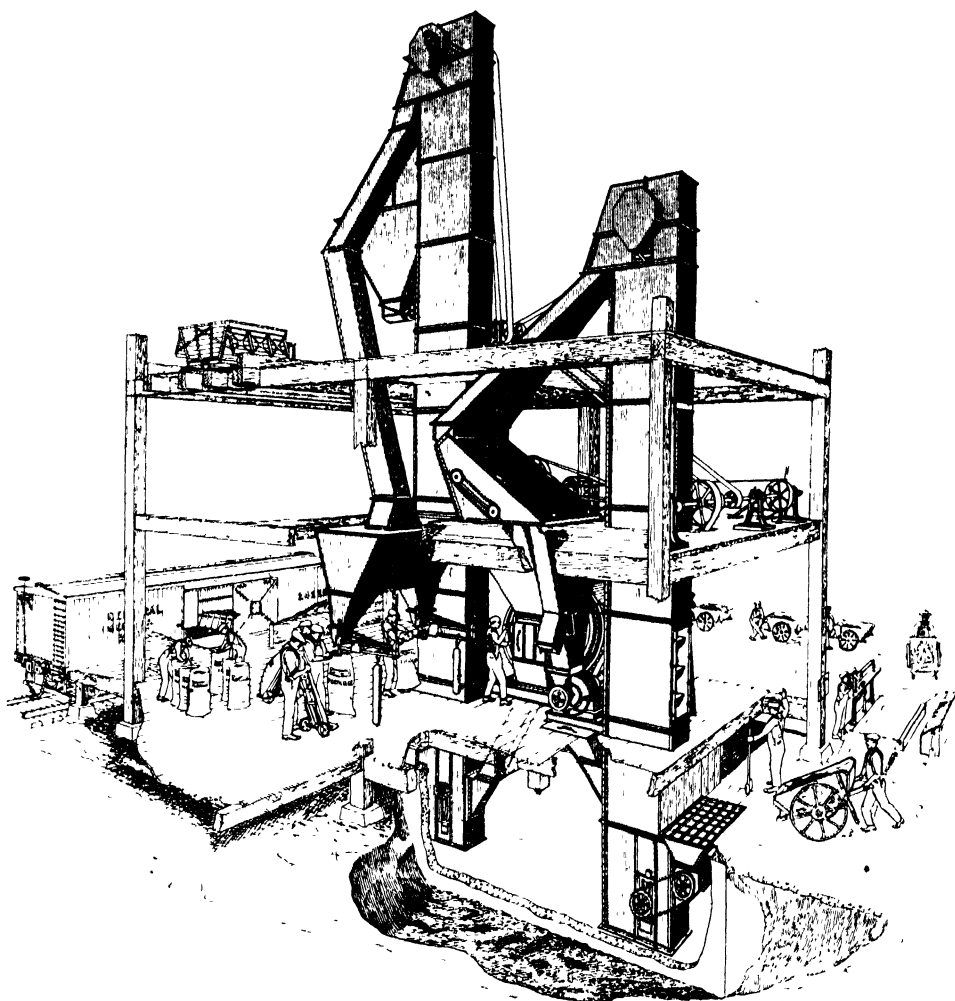


FIG. 87.—STURTEVANT MIXING AND BASING UNIT

The most popular fertiliser mixer is shown in Fig. 88. It possesses certain special features. It has only one opening for receiving and discharging its batch. There is only one opening, therefore, to seal against the escape of dust. The steel drum in this machine is supported on trunnion bearings which are mounted on a steel channel bedplate. There is a spur rim at one end of the drum, which engages with a pinion on the countershaft. The inlet and discharge shoots are attached to the same slide. When filling the mixer, a lever places the inlet shoot into the receiving position; reversing this lever brings the discharge shoot into place for emptying the machine (see Fig. 89). There is a large, easily removable door in the end of the drum opposite the feed and discharge end, which admits of quick and easy accessibility for cleaning and inspection.

Inside the drum there are a large number of scoops and deflectors, which ensure quick and intimate mixing, and allow no separation of the ingredients. These are shown in Fig. 89.

One half minute is sufficient time for mixing.

This mixer is built in various sizes, having capacities from $\frac{1}{4}$ -ton to 2-ton batches.

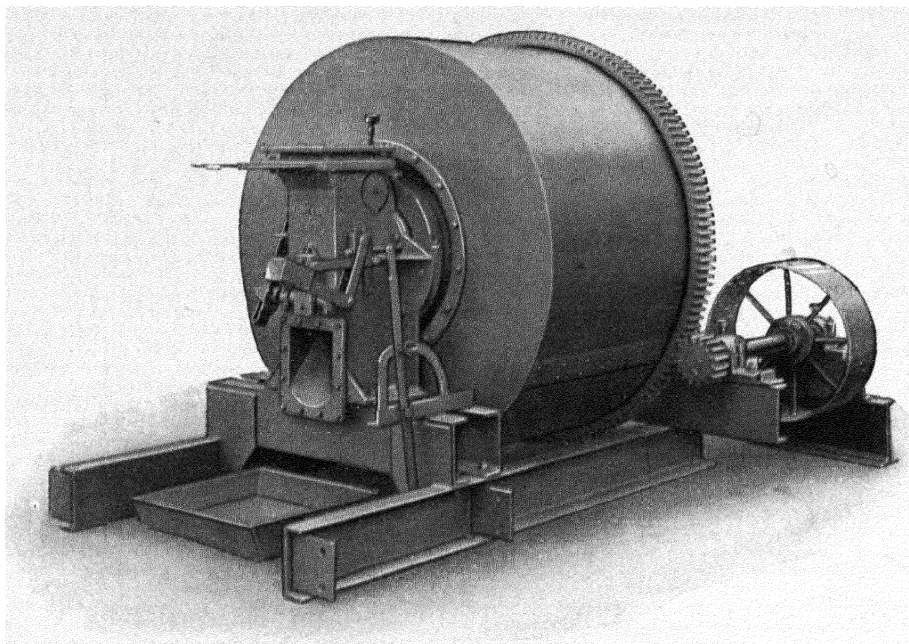
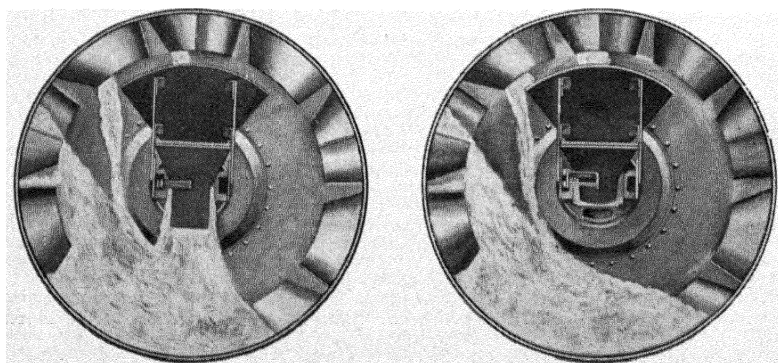


FIG. 88.—STURTEVANT FERTILISER MIXER

The 1-ton size machine, which is most extensively used, requires 8 b.h.p. for driving, and is capable of mixing 15 tons of fertilisers per hour.

Fertiliser Screens.—The screens which are used in all fertiliser-mixing units fulfil a very important function. If the screen fails to operate the whole unit becomes inefficient and inaccurate. Fertiliser materials, especially superphosphate, are not easy to screen on account of their tendency to clog. All screens used for this purpose are therefore fitted with some form of electrical or mechanical vibrating device.



FILLING

DISCHARGING

FIG. 89.—STURTEVANT FERTILISER MIXER

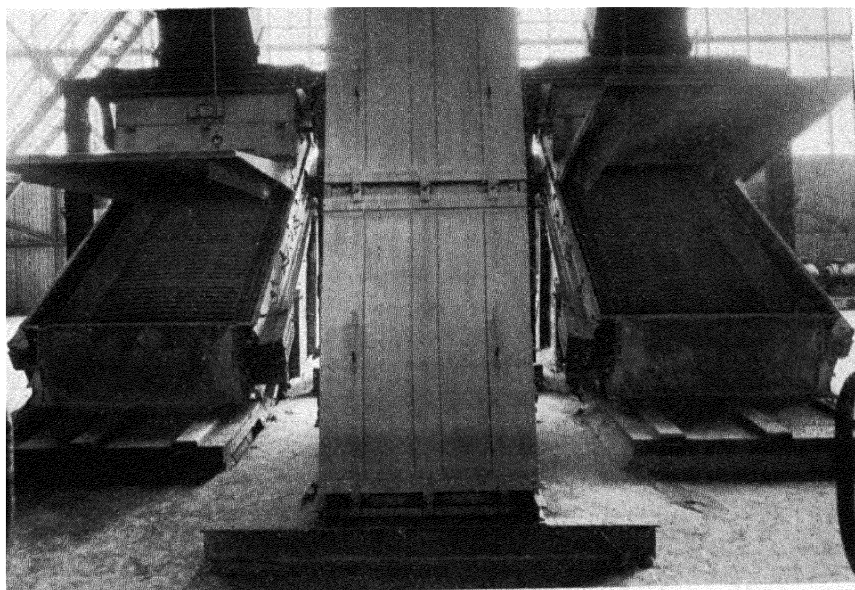


FIG. 90.—HUMMER ELECTRIC SCREENS

Hummer Electric Screen.—The screens shown in Fig. 90 represent the most recent development in screening by electric vibration.

There are four electric vibrators, one at each corner. The two vibrators at the feed end are yoked together by a cross armature beam, and so are the vibrators at the discharge end.

These armature beams are intensely vibrated and transmit the vibration to the screen cloth through the supporting screen framework. The electric vibrator delivers 1,800 short powerful strokes per minute combined with a sharp impact. The cloth is held in place by hinged plates running the full length of the screen at both sides which can be quickly swung into position to remove the screen cloth.

Each of the screens shown in the illustration, Fig. 90, has a screening area of 28 sq. ft., and when fitted with 3 mesh screen cloth will extract 15 tons per hour of matured superphosphate.

The vibrators used with Hummer screens require an alternating current supplied by a special low-frequency generator or motor generator.

The Sturtevant "B.B." screen, or "Bucking Broncho," is shown in Fig. 91. It is of the inclined type with the screen set at an angle of 35°. The screen frame is hung from the casing at the top by means of chains, and rests on two sets of cams. The cams are protected by two steel channels fixed under the screen. These cams produce sharp and violent jars and slams in numerous directions, which clean the meshes. The screen cloth is fitted to the frame in such a manner that it can be quickly renewed; the casing is provided with a hinged top for quick accessibility. These screens are usually covered with 3-mesh cloth, and a machine having 40 sq. feet of screening surface will deal with approximately 15-20 tons of fertiliser material per hour.

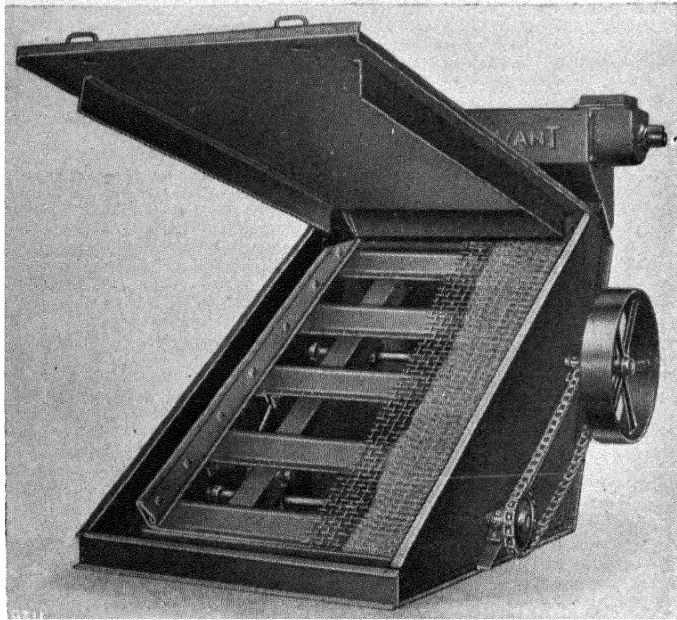


FIG. 91.—STURTEVANT B.B. SCREEN

Tailings Pulveriser.—Reference has been made to the use of such an apparatus in the various mixing units described. They are generally high-speed machines of the hammer type.

Fig. 92 shows a tailings pulveriser built on the open-door principle and fitted with hinged hammers. The flexibility of this type of hammer prevents serious damage if a piece of iron should enter the machine.

The shaft runs at a speed of approximately 1,200 revolutions per minute, and something like 24,000 blows are delivered to the material every minute, so that there is little chance of any lumps escaping.

When used as a tailings grinder only, no grates are necessary. Five b.h.p. is sufficient to drive the pulveriser as the shaft runs in self-aligning roller bearings.

The Tyler Blender. This machine combines the three operations of disintegrating, screening and mixing of fertilisers in one apparatus, but additional hand labour is involved.

It is shown in Fig. 93. It consists of a conical casing, inverted and tapering vertically downwards to a discharge outlet. Inside this cone are arranged eight fixed sieves, tapered to suit the shape of the framework, which holds them in position. When placed in position they form an inverted octagonal cone, which connects at the bottom with an outlet pipe: this pipe passes

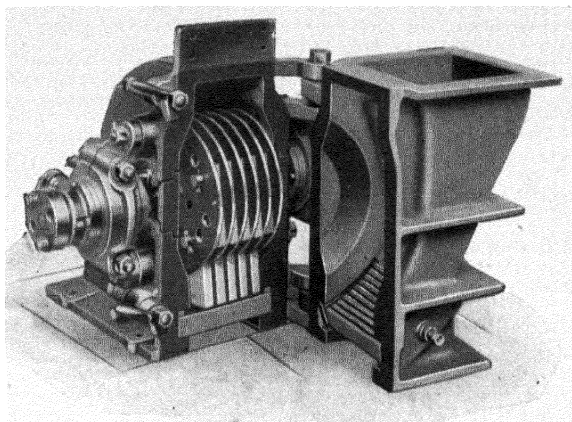


Fig. 92.—STURTEVANT TAILINGS PULVERISER

but are travelling in a spiral direction within the conical screen and falls into the outer casing, from which it is bagged at the bottom. The tailings pass downwards within the screen casing and through the outlet at the side.

Sacking Scales.—Automatic scales for the weighing of fertilisers are not extensively used in the trade owing to the difficulty in maintaining an even and regular flow of material into the scale, which is essential for accurate weighing in an automatic machine. Manually operated scales are therefore generally used.

A very simple scale is shown in Fig. 94 and combines a bag-holder and valve, which are bolted direct to the hopper. The scale is made on the steel-yard principle: the bag-holder is on one end of the single lever, and a counterweight is on the other end. The valve is a single under-cut gate, easily operated and quickly cut off. The bag-holder is fitted with a ratchet-and-pawl mechanism, which has a powerful grip to prevent slip, and is quickly released.

Fig. 95 shows a combined automatic and check weigher which is accurate, quick, and dust-proof. It is an even-armed beam scale, specially designed to deal with non-free-running materials such as fertilisers. The machine cuts off automatically when a little less than the required weight is in the sack, and the remaining material necessary for exact weight is fed into the sack by a hand-operated shaker tray which is quick in action and easily controlled by the operator. The balance is clearly shown on a dial indicator, and the beam being even-armed and very sensitive, there is a perfect check on the weighing without recourse to another scale. It will weigh four or five 2-cwt. bags per minute, and the accuracy is within one ounce or better. A large number of these machines are now in use at fertiliser works.

Bag-sewing Machines.—Mechanical sewing equipment has enabled fertiliser manufacturers to reduce

through the side of the outer casing. The vertical shaft carries two discs: the upper one has a series of cutting knives bolted thereto, and on the lower disc is fitted a plain circular plate.

The materials to be mixed are first weighed and laid on the floor in layers, one above the other, and shovelled into an elevator which delivers to the inlet shoot of the blender. They are delivered by a cone feed-plate on to the cutting knives, which are rotating at a fairly high speed. These disintegrate the materials, and also impart to the particles a spiral motion, which carries them all round the internal screen: the rotating plate immediately under the knives performs the same function, so that the materials are not allowed to fall absolutely vertically, through the screen. The fine material passes through the screen. The tailings are bagged at the bottom. The tailings pass

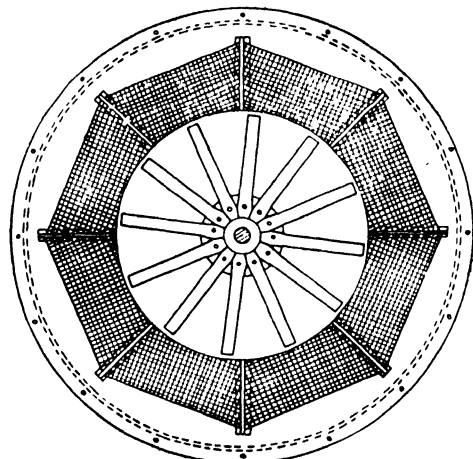
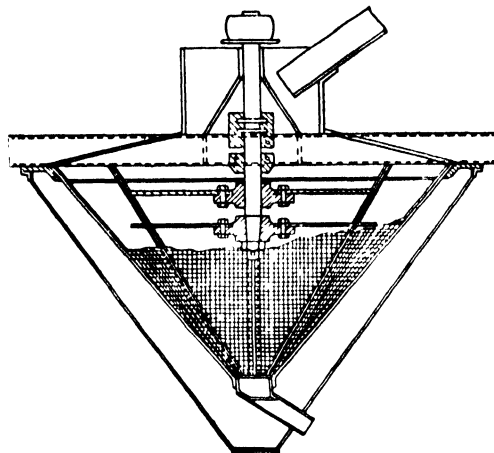


Fig. 93.—TYLER BLENDER

their costs appreciably, and at the same time provide an attractively closed sack which does not leak, and which tends to prevent caking. Machine-sewn bags do not leak and waste, hence they eliminate all complaints of short weight, and consequent expense of making good the shortage. The fact that the fertiliser is not packed so closely in machine-sewn bags allows it to work around in the bag during handling, thereby keeping it in excellent physical condition. Further, smaller bags may be used when machine-closed, which results in a saving in the purchase of bags.

The following figures, giving the costs of labour, have been collected from various works :

Where bags are sewn by hand, a trained hand sewer will close 80 bags per hour.

Where machines are in use, a machine sewer can easily close 400 bags per hour.

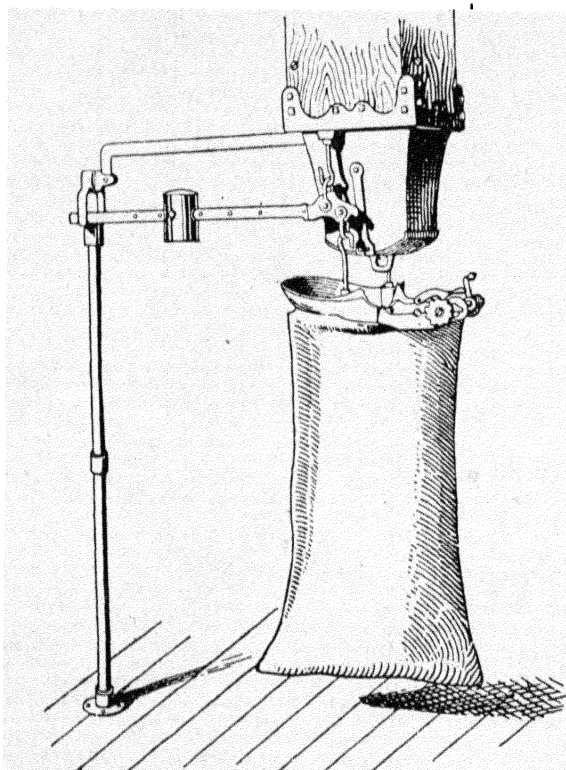


FIG. 94.—SACK WEIGHING MACHINE

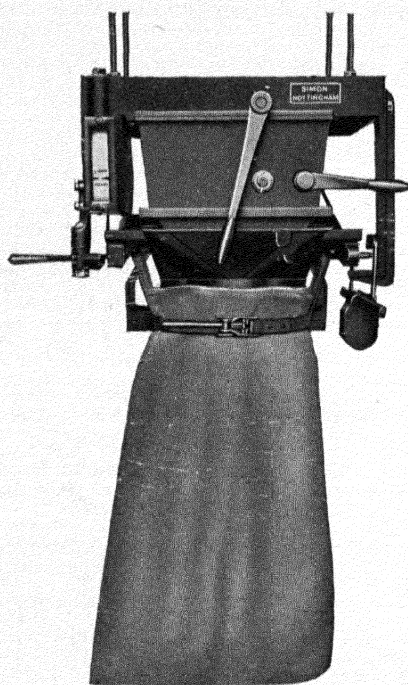


FIG. 95.—SIMON SEMI-AUTOMATIC CHECK WEIGHER

Cheaper twine can be used in the machine, so there is an appreciable saving here as well.

Where bags are sewn by hand, the labour cost rated at 1s. per hour is approximately $1\frac{1}{2}$ d. per ton.

Where bag-sewing machines are in use, the cost per ton with the same labour rate is $\frac{1}{4}$ d. per ton.

This represents a saving of $1\frac{1}{4}$ d. per ton, neglecting the saving of string.

On an output of 30,000 tons annually this represents approximately £156.

There are two types of bag-sewing machines in use, made by the Union Special Machine Company, Chicago, U.S.A.

Fig. 96 shows the conveyor type, with sewing head and conveyor in a self-contained unit. The other is used with an independently-driven conveyor.

The former type consists of a heavy frame supporting the sewing head and motor with a slat conveyor 12 to 14 inches wide and about 8 feet long. The sewing head and conveyor are driven by one motor. The driving mechanism is controlled by a foot treadle. The sewing head is adjustable up and down, to suit different heights of bags. These machines employ what is known as the double locked stitch formed with two threads and is the stitch commonly used on the sides

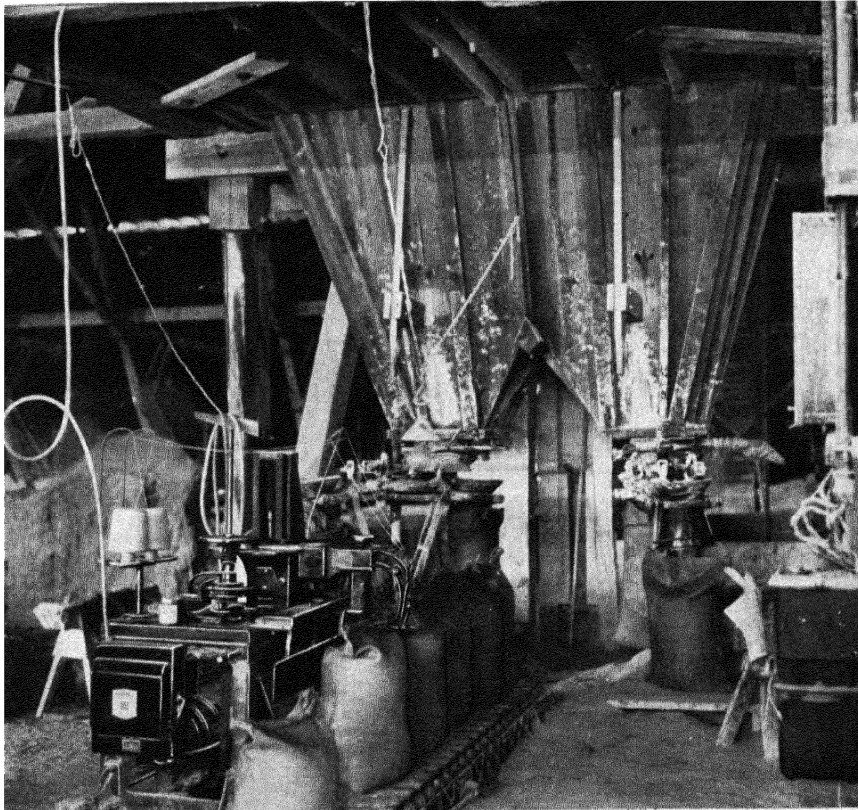


FIG. 96.—BAG-SEWING MACHINE WITH CONVEYOR

and bottom of inseamed bags. The seam is strong, secure, and elastic, yet it can be easily ravelled by separating the two threads and pulling them in opposite directions.

The equipment is generally arranged on a second floor, or on an elevated platform, so as to take advantage of gravity in dropping the sacks into railway wagons. When the conveyor is set flush with the floor, a shallow pit is arranged for the operator to stand in, to avoid continuous bending.

The power required for operating the complete mechanism varies from $1\frac{1}{2}$ to $2\frac{1}{2}$ b.h.p., depending upon the length of the conveyor.

CHAPTER XIII

THE MANUFACTURE OF PHOSPHORIC ACID AND DOUBLE SUPERPHOSPHATE

A CONSIDERATION relating to any fertiliser is the cost of transport. Naturally, with a double superphosphate, transport costs, whether by rail or water, are reduced materially. Commercial phosphoric acid is usually produced by treating finely-ground phosphate rock or bone ash with sulphuric acid. The larger proportion of phosphoric acid is manufactured from mineral phosphate.

With degreased and degelatinised bones as the raw material, the unit processes involved are (a) calcination, (b) dissolution, (c) filtration, and (d) evaporation. Where it is proposed to use a mineral phosphate as the raw material, then it will be appreciated that there is no necessity for calcination, and the unit processes are (a) dissolution, (b) filtration, and (c) evaporation.

Utilisation of Bones

Bones should be calcined, and afterwards ground in a disintegrator, and dressed through a reel having a 100-mesh wire screen. The bone ash is then fine enough for phosphoric acid manufacture.

Bone-waste residue (lumps only) from glue digesters is a material from which a suitable bone ash is prepared. This is calcined and ground as indicated above.

The process of calcination can be carried out in a simply constructed furnace. Twenty-four hours are required for each batch. Bone lumps are fed into the calcining furnace, and, when full, a wood fire is lighted under the fire-bars. The bones will ignite, and the mass gradually burn through. A good draught is necessary. There is no necessity to replenish the fire when ignition of the bones has commenced.

It is not usual to use bone ash for manufacturing phosphoric acid intended for use in double superphosphate. Bone is a valuable source when phosphoric acid is required for the manufacture of suitable products for baking and leavening purposes.

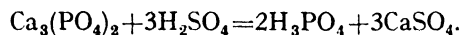
A good grade of phosphoric acid can be obtained from bones, and it requires less treatment for the removal of impurities than the phosphoric acid prepared from mineral phosphate. The impurities present—calcium sulphate, iron and aluminium compounds, fluorine, arsenic, and lead present in phosphoric acid prepared from mineral phosphate—are not usually removed from the acid employed in the manufacture of a double superphosphate.

Hence it cannot be doubted that bone is not an economical material for this purpose.

Description of the Process for the Manufacture of Phosphoric Acid for Double Superphosphate

The rock phosphate is ground to a degree of fineness equal to about 5 per cent remaining on a 60-mesh sieve. The fineness required varies with different phosphates, and has an important bearing on the efficacy of dissolution in sulphuric acid as well as filtration.

A weighed quantity of phosphate is mixed with definite quantities of water and sulphuric acid. The reaction which takes place is represented below.

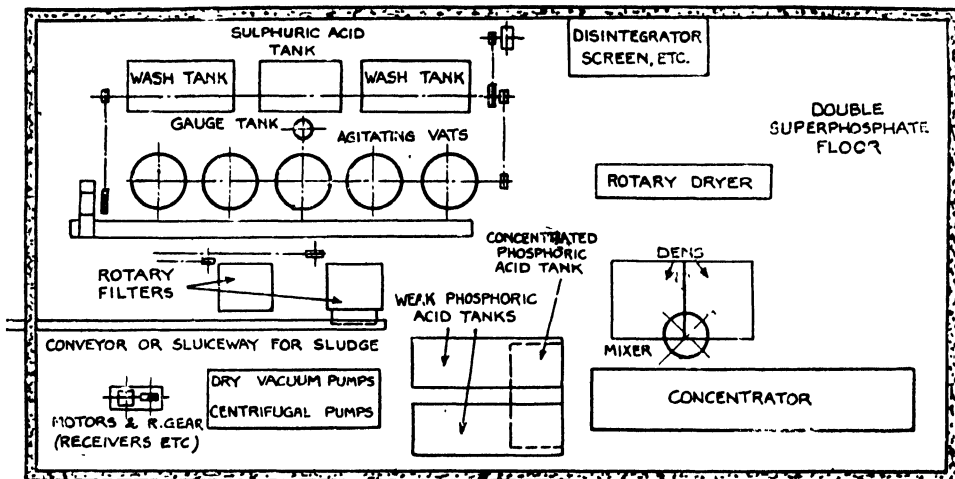


The mixing is usually carried out in lead or acid-proof brick-lined vats, with suitable stirring devices. Air agitation is not to be recommended.

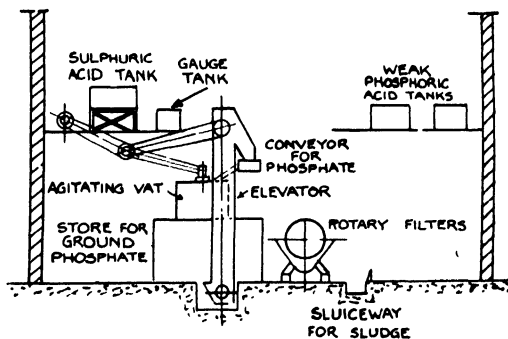
An alternative method is to treat the ground phosphate with a stronger acid, and make a superphosphate which is subsequently placed in the vat and treated with the requisite quantity of water.

This method is satisfactory, but, as will be appreciated, it entails an additional operation.

In the first method, where direct treatment of the phosphate in the agitating vat is resorted to, a longer period is necessary for complete reaction than with the alternative method. Three to five hours are required, dependent on the nature of the phosphate used.



— PLAN —



— ELEVATION —

FIG. 97.—PLANT FOR THE PRODUCTION OF DOUBLE SUPERPHOSPHATE

The plant outlined in Fig. 97 is suitable for a production of 1,000 to 2,000 tons of double superphosphate per annum.

If mineral phosphates are used, it is preferable to work on fairly high grades. Florida rock or Florida land pebble are suitable. The higher grades of Algerian phosphates also give satisfactory results.

The quantity of sulphuric acid necessary for the decomposition of the phosphate will vary according to the nature of the phosphate used. With mineral phosphates, the quantity of calcium carbonate, iron oxide, and alumina present has an important bearing on the quantity of acid used.

Filtration.—This unit process is adopted in order to effect a separation between the phosphoric acid and the insoluble calcium sulphate. The calcium sulphate can be removed by a counter-current decantation system, Dorr system, or by filtration.

Filtration is most effective. Filter presses or mechanical filters (Nordengren system) can also be used.

The mechanical filter has been developed to a fine art by the Kemiska Patentör (Landskrona), and can confidently be recommended. Further details are given later.

For a small output, the installation of filter presses may be preferable, and less expensive. For larger outputs, continuous mechanical vacuum filters are eminently suitable, and installation costs compare favourably with those for filter presses. So far as the ordinary filter presses are concerned, the type to be used is the frame press, with provision for thorough extraction.

The Oliver continuous filter is satisfactory when used for phosphoric acid solutions, and can be obtained specially constructed for the purpose, and is practically proof against the acid.

With either filter presses or continuous vacuum filters, the phosphoric acid can be removed to below 1 per cent available P_2O_5 in the calcium sulphate residue as determined on a dry sample.

Evaporation.—The most suitable type of plant for the evaporation of the weak phosphoric acid also depends on the quantity to be treated, and to some extent on local conditions. Three methods of evaporation are used.

- (a) Pans fitted with lead steam coils.
- (b) Overheat evaporators of the Porion type, or by overheat without fanner blades.
- (c) Hot-air-spraying systems.

The best system appears to be the last-named one. An acid-proof brick tower is required, provided with a suitable connection for the introduction of the products of combustion from an oil furnace.

Whether methods (a) or (b) should be used depends largely on local conditions, and whether or not exhaust steam at a suitable pressure is available, or whether or not there is a source of waste heat. The hot-air-spraying system is only applicable to large productions.

If lead coils are used, the separation of calcium sulphate from the hot solutions is troublesome. The coils become coated with hard scale, and the removal of this (which is not infrequently necessary) is somewhat destructive to the coils.

Such difficulties can be avoided with overheat evaporation, although it is necessary to clean out the pans occasionally. By adopting the last-named method, contamination from lead can also be obviated, as the concentrator can be constructed throughout with acid-proof brick.

The loss by volatilisation during evaporation is considerable, and on large installations it might be profitable to recover by means of electrical precipitation. The loss in question is slightly less with (a) than with (b).

The foregoing represents the technique in this country up to 1926. Since that time Nordengren and his collaborators have undertaken much work, the primary object of which was to evolve a cheap method for producing phosphoric acid to be used for the enrichment of superphosphate. Dr. Lehrecke contributed details of this development to a meeting of the International Superphosphate Manufacturers' Association in Hamburg on October 12, 1937, and what follows is the English translation of that contribution, which was prepared by one of the authors (Parrish) for publication in the *Chemical Age* of October 30, 1937.

The work begun by Nordengren and his collaborators in Landskrona in 1926 had for its primary object the discovery of a cheap method of producing phosphoric acid, to be used for the enrichment of superphosphate. In Sweden at the time it was the practice to mix high-grade

South Sea phosphates or Curaçao phosphate, with Florida or African phosphates, in order to produce a calcium superphosphate containing 20 per cent of P_2O_5 . The continuance of this method was threatened by reason of the progressively diminishing quantity of high-grade phosphates available.

Before the enrichment process with phosphoric acid was conceived, it will be recalled that the question was raised, whether it would be possible to increase the P_2O_5 content of the superphosphate by reducing the water of crystallisation of gypsum ($CaSO_4 \cdot 2H_2O$). It was believed then that superphosphate contained gypsum, as distinct from anhydrite ($CaSO_4$), or the hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$). As the investigations proceeded at Landskrona, it became evident that the foregoing view was erroneous, and that calcium sulphate is largely present in superphosphate, essentially as anhydrite. Despite the fact that no announcement was made at the time of this significant result, it will be interesting to record that the precise form in which calcium sulphate existed in superphosphate was revealed by the investigations conducted by Nordengren and his collaborators. In view of what has been remarked, it was obvious that the phosphoric acid content of calcium superphosphate could not be increased by eliminating or reducing the water of crystallisation of gypsum, and that some alternative method was called for. A method of enriching superphosphate by incorporating phosphoric acid as such during mixing had much to commend itself, and on reflection it was decided that this method should be pursued. The idea of manufacturing superphosphate in this way was not unknown. Indeed, it was appreciated that it could be undertaken without any technical difficulties, provided the phosphoric acid was available in a sufficiently concentrated form.

The problem to be solved was the production of phosphoric acid having a concentration of at least 30 per cent P_2O_5 from sulphuric acid of 54-55° Bé. The concentration in question was necessary in order to avoid an unduly high moisture content in calcium superphosphate. Phosphoric acid of the required strength had hitherto only been produced by thermic methods, but such a way could not be contemplated by reason of considerations of cost.

The "wet" methods available did not admit of phosphoric acid being produced of a greater concentration than 22-23 per cent P_2O_5 , and as such methods were based on the decantation principle, the plants and buildings were alike expensive and unwieldy. The principle of decantation for separating the insoluble calcium sulphate was abandoned at the outset, and Nordengren and his collaborators directed their efforts to evolving a method by which phosphoric acid containing at least 30 per cent P_2O_5 could be manufactured direct, the calcium sulphate being separated from the phosphoric acid by a process of filtration. A process on the foregoing lines was soon developed, and the first phosphoric acid plant was built at Landskrona in 1928.

The Autoclavic Process

The process, as originally evolved (it has since been abandoned), consisted of a reaction between phosphate rock and sulphuric acid, in the presence of phosphoric acid circulated in the process, in an autoclave. It was based on the newly discovered principle that crystals of excellent condition, allowing of easy filtration, could be produced when calcium sulphate was formed under carefully regulated conditions of temperature and concentration as hemihydrate or anhydrite. Moreover, it was revealed that it was possible so to regulate the reaction that this crystalline formation remained unchanged during the filtration and washing processes, without any tendency to hydration. The required temperature of reaction, viz. 125° C. and upwards when the concentration of phosphoric acid was about 30-35 per cent P_2O_5 , could obviously only be attained in pressure vessels of the type of an autoclave.

The first installation worked intermittently with two autoclaves: the acids employed, but not the autoclaves, were heated. The plant had a comparatively small capacity: filtration was effected in a peculiarly simple manner in wooden boxes, lined with lead, the thickness of the filter cake being about 8 inches. Counter-current washing of the cake was resorted to, and it was found very effective. The cake was removed by hand, and during this procedure the jute filter cloth was destroyed.

Landskrona Belt-Filter

While the foregoing temporary method of working served its purpose, it was appreciated that any large-scale process would necessitate a mechanical device involving less manual work, and the use of less filter cloth. During the period 1930-32 many types of mechanical filters were operated in the hope that sooner or later it would be possible to construct one that incorporated most of the essential features called for in connection with the newly developed process.

The filtration, on a large scale, of a warm phosphoric acid-containing sludge with such a high concentration of P_2O_5 is a more onerous unit process than is usually encountered in chemical engineering. The features which an ideal mechanical filter should possess may now be indicated:

- (1) Continuous operation, requiring only a minimum of supervision.
- (2) Ability to resist the corrosive influences of warm phosphoric acid of high concentration, containing small amounts of the derivative products of fluorine and free sulphuric acid.

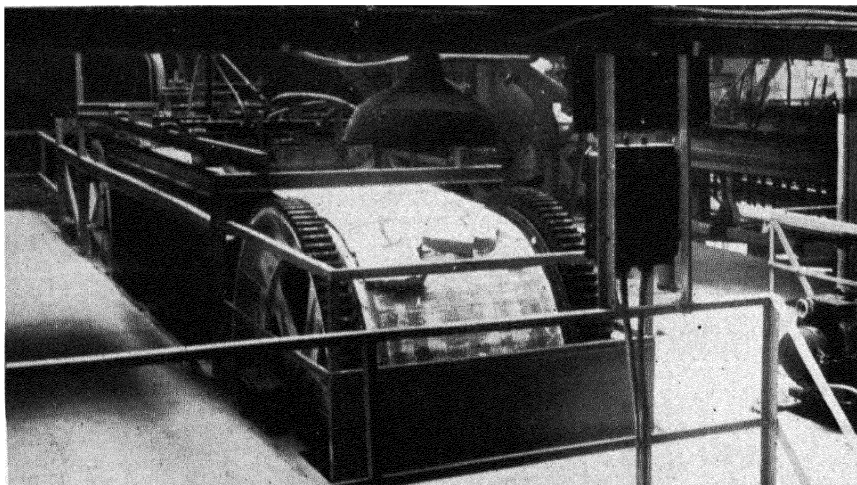


FIG. 98.—LANDSKRONA BELT-FILTER WORKING IN A BELGIAN PHOSPHORIC ACID PLANT

- (3) Complete separation of the calcium sulphate from the mother liquor: counter-current washing of the calcium sulphate to ensure practically complete elimination of the occluded phosphoric acid, with minimum dilution.
- (4) Filter cake of uniform thickness, free from surface cracks.
- (5) Ability to use a high vacuum, in order to obtain a dry filter cake.
- (6) Construction without narrow passages, and easy access to all parts for cleaning purposes.
- (7) Continuous cleaning of the filter cloths during the process of filtration in order to maintain the throughput of filtration, and to ensure high durability of the texture.
- (8) Flexibility in the production of different washing fractions in order that varying qualities of phosphate rock can be suitably treated.

All the foregoing stringent conditions are fulfilled by a new type of filter, developed at Landskrona and introduced to the industry under the name of the Landskrona Belt-Filter. As will be appreciated from this name, the process of filtering is combined with the transport of the sludge or the filtercake on belts. There are two belts: the under-belt has a channel, or disc section, and carries another perforated belt on which, in turn, the filter cloth is supported. The under-belt,

throughout the length between the pulleys, passes over a long narrow suction box that can be divided into sections, each taking a fraction of the filtrate. The first technical filter was installed at Landskrona in 1932-33. Figs. 98 and 99 each show a 5-metre-square filter, which were delivered respectively to Belgian and Dutch phosphoric acid works. The adaptability of the Landskrona Belt-Filter to other filtering propositions, especially such as are combined with the washing of the cake, is at once obvious. Indeed, this special filter has been applied for a variety of purposes. Moreover, the Landskrona Belt-Filter has also been employed for reducing the water content of sludges, as in the preparation of ores, etc. This is a typical example of how the solution of a technical problem can be applied with advantage to other fields of work.

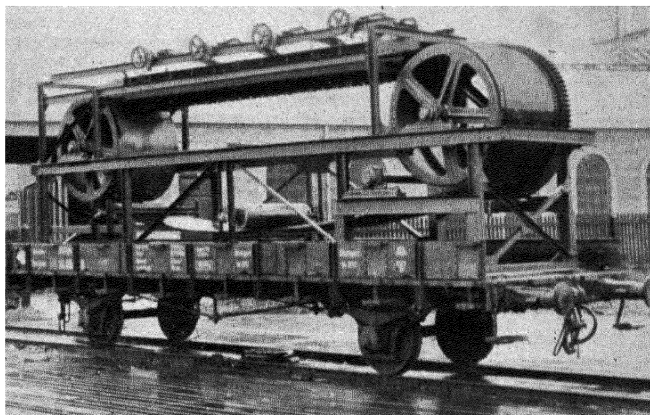


FIG. 99.—LANDSKRONA BELT FILTER FOR A DUTCH PHOSPHORIC ACID PLANT

Open Anhydrite Process

Concurrently with the demand for the construction of a special mechanical filter, adapted to plants of greater capacity, the question arose whether in larger plants it would be possible to dispense with the autoclavic process, which had the disadvantage that not only did it involve expensive installations, but it was not continuous in operation. A profound investigation was undertaken of the laws governing the conditions in which calcium sulphate containing less than two molecules of water, in the case of gypsum, existed in phosphoric acid at different temperatures and concentrations of P_2O_5 . The results are shown in diagram, Fig. 100. On the abscisse are the P_2O_5 concentrations in the reaction mass, and on the ordinate are the temperatures. The curve A shows the conditions under which such hemi-hydrate, still possessing the power of absorbing water, as water of crystallisation, is formed. Under this curve, gypsum—the di-hydrate—is stable. Curve B shows the conditions that lead to stable hemi-hydrate. In the field above this curve is situated an area where the stable anhydrite can be formed. This is the same form of calcium sulphate as we find in superphosphate.

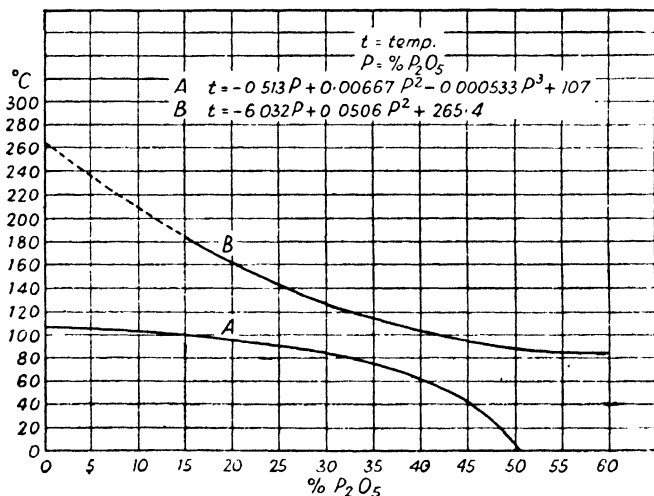


FIG. 100.—GRAPH SHOWING RESULTS OF OPERATION OF LANDSKRONA PROCESS

From this diagram it is clearly seen why it is necessary to work in autoclaves with phosphoric acid at concentrations of 30-35 per cent P_2O_5 , when calcium sulphate of low water of crystallisation, in a stable form, is demanded, because under such conditions temperatures of at least 115-127° are reached (see Curve B). If, however, the concentrations of phosphoric acid are further increased, it is possible to reduce the temperature, and at a concentration of about 38 per cent P_2O_5 an area is reached where the reaction temperature is lower than the boiling point of the solution. Hence it is possible, at these high concentrations, to allow the reaction to take place in open vessels.

To work in such a way it was necessary to dispose of a circulating phosphoric acid, with a concentration of adequate strength, and to produce such an acid of such a concentration, as a second filtrate, at the filtering process. Only in this way was the use of sulphuric acid of 60° Bé., or of lower concentrations, say, 58° Bé., feasible. The development of the new filter admitted of the realisation of what was demanded, in that this circulating phosphoric acid, within the filtering process, can be produced with a P_2O_5 content only 4 per cent less than the content of the product obtained.

Based on these fundamental conditions, and aided by the technical means thus rendered available, the so-called anhydrite process was tried out. It was found possible to produce a phosphoric acid with 40-45 per cent P_2O_5 in open vessels. The reaction can be carried out either continuously or intermittently. In the first case, three-four reaction tanks are used, the first two being heated. From the last tank, the pulp is pumped to the belt-filter. Here the acid is withdrawn, and the calcium sulphate is washed in counter-current with three washes, two containing acid of weaker concentration, and the other water. The yield of the washing process is 98 per cent or more, and the overall yield of the process is more than 94 per cent.

Initially, the process caused some difficulties, the chief of which was the inability to obtain a filter cloth having adequate resistance. The common filter cloth was incapable of withstanding the strong warm phosphoric acid. It was ultimately found necessary to use nitrated cloth, which at the time was not easy to obtain. Now it is possible to buy a nitrated strong cotton cloth without difficulty, and at a reasonable price.

The anhydrite process is the only one that admits of phosphoric acid of 40 per cent P_2O_5 or more being produced direct from any variable phosphate rock on the market, and sulphuric acid. It should be remarked that the phosphate rock need not necessarily be ground finer than for the production of superphosphate.

Evaporator

If double superphosphate is to be manufactured from phosphate rock and phosphoric acid, a concentration of 40-45 per cent P_2O_5 in the acid is not sufficiently high; indeed, a concentration of at least 50 per cent P_2O_5 is essential. With such an acid, double or triple superphosphate can be manufactured in the same way, and in the same plant, as ordinary superphosphate, and there will be no necessity to dry the product. From this viewpoint investigations were conducted as to how phosphoric acid of different strengths could be concentrated with facility, and at a minimum cost. When technical acids are being evaporated, difficulties arise because the calcium sulphate and other impurities precipitate as the concentration of P_2O_5 increases, and such precipitate adheres to the walls or pipes of the evaporator, rendering the transmission of heat difficult, and withal occasioning considerable work in the matter of cleaning.

An evaporator should be constructed in such a way that depositions of calcium sulphate are avoided, or at least only occur at such points which admit of easy cleaning, and where no damage can be done.

These were the considerations that one had in mind when the new evaporator was constructed, using heated gases, which are blown through the acid, as the source of heat, rather than steam. Such heat may be obtained free of cost in superphosphate plants having sulphuric acid installations, where the pyrites furnaces are cooled with air. The air is discharged from the furnaces at a temperature of 250-300° C., usually into the atmosphere. The new evaporator has specially constructed lead-lined mouthpieces, through which the heated air is blown with the aid of a fan, giving a pressure of 150-200 mm. (water pressure). Gases are discharged at a tolerable velocity under the surface of the phosphoric acid. The construction of the mouthpiece affords highly effective heat transmission, and the gas temperature at the outlet is only a few degrees higher than the temperature of the acid (60-70° C.). The power necessary for the evaporation of 1,000 gallons of water in 24 hours is only about 4.4 h.p., so that when heat is available free of cost, the evaporation is inexpensive. One is not limited to the one source of heat indicated; combustible gases as a source of heat, with the admission of air, give a satisfactory temperature, and, of course, air can be heated in other ways to advantage.

The supervision and cleaning of the plant only involve a relatively small amount of time. The feed of acids, as well as their concentrations, is from time to time controlled by one man,

who also, once a day, cleans the mouthpieces. Each week a thorough cleaning of the equipment is undertaken. The waste gases are led to a scrubber, where the fluorine compounds are absorbed in water. In the plant installed at Landskrona, which is shown in Fig. 101, 3 to 4 tons of P_2O_5 daily are concentrated, from 30-50 per cent P_2O_5 .

Open Dihydrate (Gypsum) Process

In view of the inexpensive method of concentrating phosphoric acid which had been developed, the question arose whether it would not be an economic proposition to manufacture phosphoric acid of lower strength, and subsequently resort to concentration in the evaporator. Under such conditions it would obviously be cheaper to effect the decomposition in open vessels without heating.

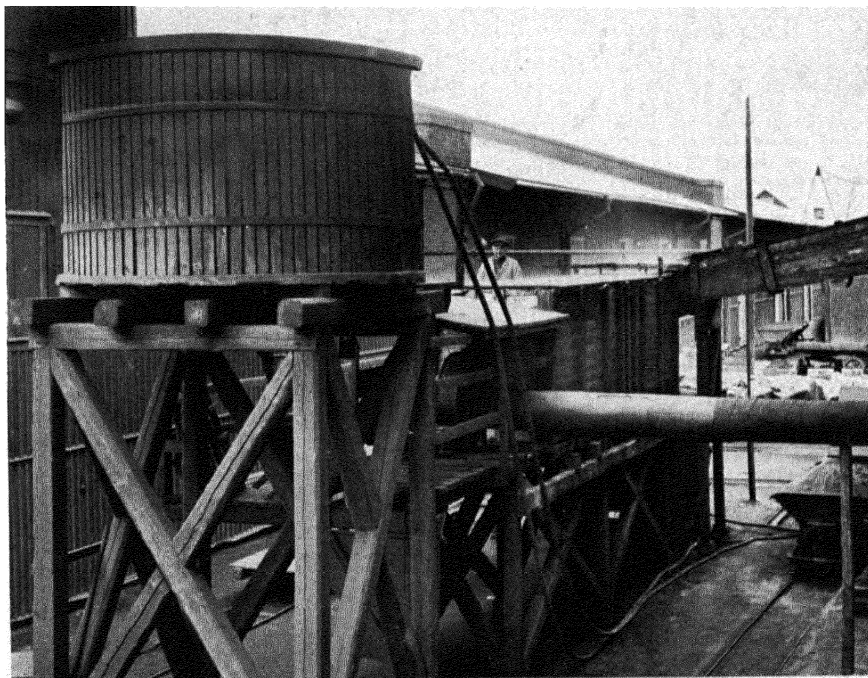


FIG. 101.—LANDSKRONA PHOSPHORIC ACID EVAPORATOR

A glance at the diagram, Fig. 100, reveals that this is only possible if calcium sulphate is formed as gypsum.

With the older methods of decomposition the calcium sulphate was precipitated as gypsum, but it was only possible to produce acids of 22-23 per cent P_2O_5 in a direct way. This was attributable to two causes: (a) separation by decantation, by which the mother liquor became diluted; and (b) at higher concentrations poorly or not easily filtrable crystals of gypsum were obtained.

Thorough investigation has now revealed that it is possible to increase the concentration of the phosphoric acid up to 30 per cent P_2O_5 , and simultaneously obtain excellent crystals of calcium sulphate as dihydrate, allowing of easy filtration, if the decomposition is regulated in a suitable manner. The factors governing the foregoing are (a) temperature and concentration; (b) the proportion of the components; and (c) the way in which these are charged. Another condition

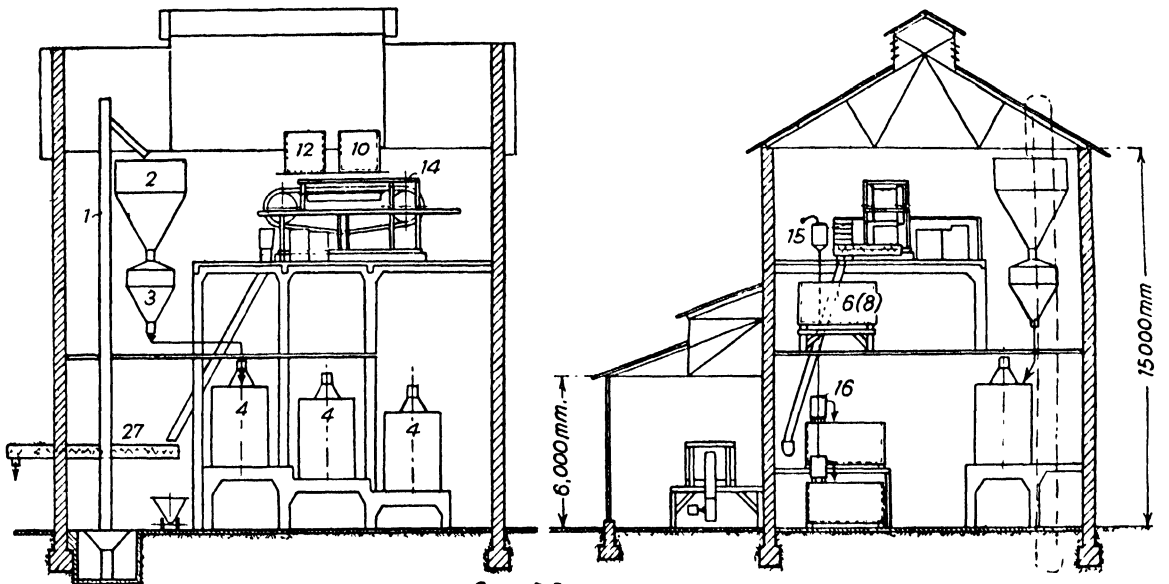
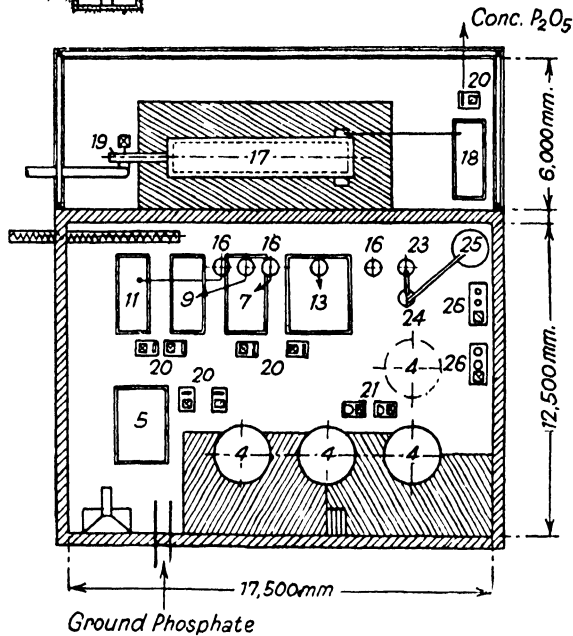


FIG. 102.—LAYOUT OF LANDSKRONA PHOSPHORIC ACID PLANT



1. Elevator for ground phosphate.
2. Bin for ground phosphate.
3. Balance (Poidometer) for ground phosphate.
4. Agitators (3 resp. 4).
5. Tank for sulphuric acid.
6. Tank for sulphuric acid.
7. Tank for circ. phosphoric acid.
8. Tank for circ. phosphoric acid.
9. Tank for wash acid I.
10. Tank for wash acid I.
11. Tank for wash acid II.
12. Tank for wash acid II.
13. Tank for product.
14. Bandfilter.
15. Vacuum recipient.
16. Acid trap.
17. Evaporator.
18. Tank for conc. phosphate acid.
19. Hot air ventilator.
20. Pumps for acids.
21. Pumps for sludge.
22. Acid distributor.
23. Washing scrubber for waste gas.
24. Spray catcher.
25. Vacuum tank.
26. Vacuum pumps.
27. Screw transporter for gypsum sludge.

A. B. KEMISKA PATENTER, LANDSKRONA, Sweden.

SCHEME OF A PHOSPHORIC ACID PLANT WITH HOT AIR EVAPORATOR

Capacity by batch operation with 3 agitators and 1 evaporator unit 5 tons P_2O_5 in 24 hr. as 50 per cent solution
 Capacity by continuous operation with 4 agitators and 2 evaporator units 10 tons P_2O_5 in 24 hr. as 50 per cent solution.

necessary to admit of the attainment of such concentration, with the possibility of obtaining strong acids of easy filtration, is an equipment possessing the features of the belt-filter. It will be appreciated that it is not necessary, in this process, to heat the decomposition vessels, nor indeed the acids. The filtering process can be performed with the usual wool cloth, and it is very cheap, as only 0.3-0.4 square metre is destroyed per 100 kgms. of P_2O_5 produced. As regards washing, only one wash is required, except the water one. Phosphoric acid is produced, containing 25-30 per cent of P_2O_5 , dependent on the quality of the phosphate rock treated. The process can be worked continuously or intermittently, with all qualities of phosphate on the market. Indeed, African phosphate, which hitherto has generally caused difficulties, can be used. The total yield is 94 per cent or more.

A schematic outline of a phosphoric acid plant for the production of 10 tons of P_2O_5 per twenty-four hours, according to the method in question, is shown in Fig. 93. The decomposition unit is, in point of size and arrangement, also suitable for the anhydrite process, having a corresponding capacity. The volume of the decomposition vessels, per thousand kgms. production of P_2O_5 per twenty-four hours, is small, and corresponds to 3-5 cubic metres for the dihydrate process, and 4-6 for the anhydrite process, according to the quality of phosphate rock used.

Again, for the production of phosphoric acid that does not aim at higher concentrations than can be reached in the dihydrate process, as for example, phosphoric acid to be used for the production of sodium and ammonium compounds, the process now described combines simplicity of design and cheapness of operation that can scarcely be excelled.

The investigatory work affecting the production of phosphoric acid from the decomposition of phosphate rock with sulphuric acid, that began in 1926, by Nordengren and his collaborators, has now been consummated, after a period of ten years. Theoretical assumptions have been thoroughly investigated, and practical methods of working have taken definite forms. The technical possibilities that have been developed are the following :

- (1) Anhydrite Process : direct production of phosphoric acid containing 40-45 per cent P_2O_5 , in open vessels, with heating. Application : enrichment of superphosphate, production of salts, etc.
- (2) Anhydrite process with concentration of product to more than 50 per cent P_2O_5 . Application : double and triple superphosphates, enrichment of superphosphates, etc.
- (3) Dihydrate process : direct production of phosphoric acid containing 25-30 per cent P_2O_5 , in open vessels, without heating. Application : phosphoric acid salts, phosphate of ammonia. Enrichment of superphosphate.
- (4) Dihydrate process with concentration of product to more than 50 per cent P_2O_5 . Application : double and triple superphosphates. Enrichment of superphosphates, etc

According to circumstances, one or other alternative should be preferred. All alternatives can be worked continuously or intermittently, according to the size of the plant. The installation would in all cases be relatively simple, and contrasted with older decantation plants, would not involve anything approaching the original installation costs, and would occupy only a fraction of the space formerly necessary. The plant can be put out of action at will, and can be restarted in a very short time, as only comparatively small amounts of acid and sludge are circulating, or are present.

The essential conditions that admit of the production of technical phosphoric acid are (a) that calcium sulphate must be in a form allowing of easy filtration ; and (b) the filter must be so constructed that it is possible to separate the acid economically, without unnecessary dilution occurring. These conditions, as has been remarked, have been attained, and it is now possible to produce phosphoric acid of high concentration, so cheaply—at least, in larger plants—that double or triple superphosphate can be manufactured at such prices per unit of P_2O_5 , as to approach very nearly that of the unit price of P_2O_5 in superphosphate. Moreover, the slightly higher cost can practically be disregarded, in view of the lower costs of transportation and packing.

Other processes that call for consideration are the continuous counter-current decantation principle of the treatment of phosphate rock with sulphuric acid—the one associated with the Dorr

Company. Although the cost of this plant is generally regarded as heavy, labour charges are economised, and the overall efficiency of the process is remarkably high.

Phosphate rock is ground initially to admit of 90 per cent passing an 80-mesh screen. The phosphate, with a predetermined proportion of sulphuric acid, is introduced into a series of four lead-lined mixing-vats, equipped with stirring devices. The materials are preliminarily mixed, and reaction occurs. Sulphuric acid drawn from the chambers, diluted to 27-30° Bé. (46.2°-52.6° Tw.) with 16°

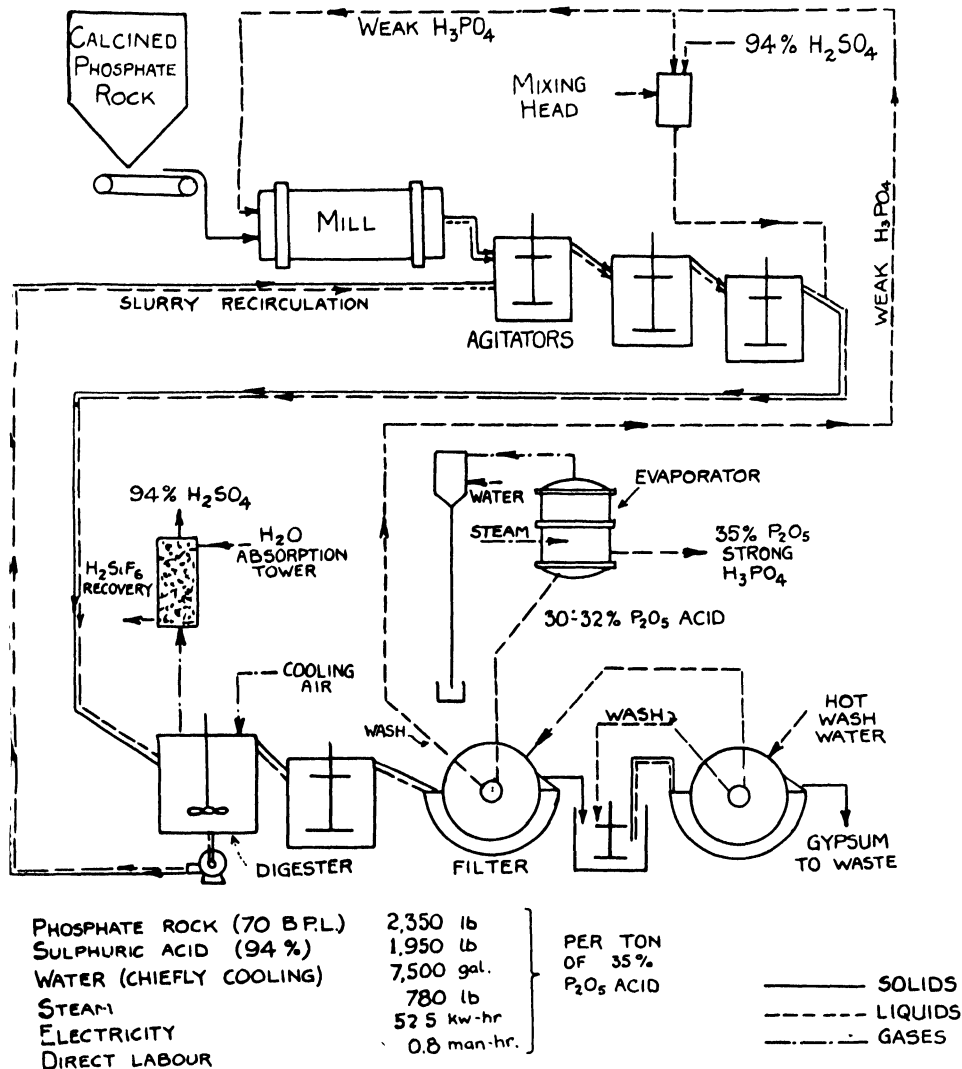


FIG. 103 -- DIAGRAMMATIC LAYOUT OF DORR STRONG ACID PROCESS

Bé. phosphoric acid (20.8 per cent H₃PO₄), obtained from the second of a series of Dorr thickeners, is employed. The dilution and reaction raise the temperature of the solutions to boiling-point, Following the preliminary incorporation, the contents of the vats are discharged to the first of a series of four agitating tanks. The Dorr agitator tank for phosphoric acid is specially equipped, and is well known. In these agitator tanks the decomposition of the phosphate is completed, and the material from the first tank is discharged continuously into the second, the second into the third, and so on.

The decomposition period is about six hours, but this is governed by (a) the quality of the rock phosphate and (b) the rapidity of the reaction.

A peripheral tray collects the relatively clear phosphoric acid, 27° Bé. (35.8 per cent H_3PO_4), which overflows from the top tank and is fed to the evaporators to be concentrated.

The saturated residue discharged from the base of the first thickener is pumped to the second, and the overflow from this second thickener, which has a concentration of 15-16° Bé. (19.5-20.8 per cent H_3PO_4), is pumped to the pre-mixers, where it is employed for the dilution of the chamber acid used at the start of the process for effecting the decomposition of the rock phosphate. The flow sheet, Fig. 104, is the best and most graphic means of representing the application of the Dorr continuous counter-current system of phosphoric acid manufacture. It reveals the strength of the phosphoric acid in each successive thickener.

It is claimed that an extraction of over 99 per cent of the P_2O_5 content of ordinary phosphate rock can be effected by the Dorr system. But practical experience suggests that 95 per cent is an average works figure.

Fig. 103 shows a diagrammatic layout of the Dorr strong acid process, the object of which is to economise space, equipment, the quantity of phosphoric acid in process, buildings, and to make a stronger phosphoric acid and therefore reduce costs of evaporation to a minimum. Indeed, only in special circumstances is it likely that the Dorr continuous counter-current system of phosphoric acid manufacture would be installed to-day. This latter process would, for the most part, be supplanted by the strong acid process.

An important paper on "The Chemical and Physical Properties of strong phosphoric acids" was contributed to the American Institute of Chemical Engineers by C. B. Durgin, J. H. Lum and J. E. Malowan. From this paper¹ the following subject-matter has been extracted :

"Phosphoric acids of greater phosphorus pentoxide content than that corresponding to orthophosphoric acid have been produced by either dissolving phosphorus pentoxide in less water than is theoretically required for the formation of the ortho-acid, or by dehydrating the latter or its acid salts. Some of the strong or polyphosphoric acids of high phosphorus pentoxide content which have been reported in the literature are listed in the following table.

TABLE 39

Polyphosphoric Acids

Acid.	Formula.	Molal ratio P_2O_5/H_2O .	P_2O_5 content . per cent. by weight.
Orthophosphoric	H_3PO_4	0.33	72.43
Triterohexaphosphoric	$H_7P_3O_{11}$	0.43	77.16
Pyrophosphoric	$H_4P_2O_7$	0.50	79.76
Penterohexaphosphoric	$H_5P_3O_{10}$	0.60	82.55
Tetraphosphoric	$H_6P_4O_{13}$	0.67	84.01
Hexerohexaphosphoric	$H_8P_6O_{19}$	0.75	85.53
Decaphosphoric	$H_{12}P_{10}O_{31}$	0.83	86.79
Metaphosphoric	HPO_3	1.00	88.74
Octerohexaphosphoric	$H_4P_6O_{17}$	1.50	92.20
Ennerohexaphosphoric	$H_2P_6O_{16}$	3.00	95.94

¹ *Amer. Inst. Chem. Eng., Trans.* Vol. xxxiii, 1937.

Many of these concentrated acids have never been positively identified and may merely represent theoretical combinations of phosphorus pentoxide and water. Pyro- and metaphosphoric acids have been available in small quantities, but only orthophosphoric acid has been manufactured commercially. Recently acids of high phosphorus pentoxide content, equivalent to pyrophosphoric and tetraphosphoric acids, have been introduced as commercial products.

Although the physical characteristics of orthophosphoric acid are well known and pyro- and metaphosphoric acids have been partially studied, little has been published on phosphoric acids containing more than 72.4 per cent of phosphorus pentoxide, equivalent to 100 per cent orthophosphoric acid.

Solidification Characteristics

In Table 40 are compared the solidification characteristics of phosphoric acids of high phosphorus pentoxide content.

TABLE 40
Solidification of Strong Phosphoric Acids

Acid.	P ₂ O ₅ content. Weight per cent.	Solidification characteristics.
Orthophosphoric . . .	72.43	May remain liquid at room temperature for a considerable length of time. Solidifies immediately at 0° C. or when seeded.
Pyrophosphoric . . .	79.76	Solid crystals formed at room temperature on standing or seeding.
Tetraphosphoric . . .	84.01	Does not crystallise at low temperatures, even when seeded or agitated.
Metaphosphoric and stronger acids . . .	89—94	Glassy solids.

The phosphoric acid containing approximately 84 per cent phosphorus pentoxide does not crystallise at temperatures as low as minus 50° C. This result is in contrast to a statement by Rakuzin and Arseniev,¹ who reported that crystals of tetraphosphoric acid were obtained when the acid was permitted to stand at room temperature for five days.

“A description by Rakuzin and Arseniev of the solid phase indicates that the reported crystals were actually pyrophosphoric acid; this lower strength acid might have been formed by the absorption of moisture from the air. Experiments by the authors indicate that crystallisation of tetraphosphoric acid cannot be obtained by cooling, seeding or by agitation for extended periods of time.”

¹ Rakuzin, M. A., and Arseniev, A. A., *Chem. Zeit.*, 47, 195 (1923).

Work on the hydrolysis of strong phosphoric acids has been undertaken by the foregoing authors, and the summary of the hydrolysis experiments is indicated below :—

- (1) Metaphosphoric acid hydrolyses at a much greater speed than pyrophosphoric acid.
- (2) Metaphosphoric acid yields some pyrophosphoric acid on hydrolysis, according to the analytical results. This is not in agreement with the results of Baraleff¹ and Travers and Chu ;² Fuchs,³ however, reached a similar conclusion.
- (3) The rate of hydrolysis increases rapidly with increase in temperature. For instance, increasing the temperature of the acid from 50° to 70° C. decreased the time required for hydrolysis from 90 minutes to less than 22 minutes.
- (4) If acids of 82 to 84 per cent phosphorus pentoxide content, now available in commercial quantities, are diluted with water to approximately 54.3 per cent phosphorus pentoxide content, i.e., 75 per cent orthophosphoric acid, without cooling and under approximately adiabatic conditions, the temperature of the solution will rise to 120-140° C. and the hydrolysis will be completed in less than two minutes."

From the same paper the following table of densities of strong phosphoric acid has been culled :—

TABLE 41

Densities of Strong Phosphoric Acids

P ₂ O ₅ , weight per cent.	Density at 36.1° C.	Density at 51.5° C.	Coefficient of cubical expansion.	Density at 20° C.
72.28	1.848	1.836	0.000423	1.861
79.64	1.981	1.970	0.000361	1.992
83.93	2.046	2.033	0.000415	2.060

The electric furnace for the production of phosphoric acid has been, and is continuing to be, developed by the Tennessee Valley Authority. It is a process that should be examined by prospective phosphoric acid manufacturers, as representing what is possible on a large scale, given cheap electric power, by an entirely new method, which does not contemplate the use of sulphuric acid. Waggaman and Easterwood have dealt with this process in detail, and H. A. Curtis, of the Tennessee Valley Authority, has published many articles during the last few years in the *Chemical and Metallurgical Engineering* (New York), on the subject of his special process. For further and more detailed information concerning the volatilisation process, readers are advised to make reference to the foregoing literature.

Double Superphosphate

Double superphosphate is a highly concentrated fertiliser, invariably prepared by treating in two stages, double the quantity of phosphate rock, as contrasted with the ordinary calcium superphosphate. From the view-point of its concentration, it should be termed "triplesuperphosphate," since it contains about three times the quantity of P₂O₅ that calcium superphosphate contains, made in the ordinary way.

¹ Baraleff, D., *Z. anorg. Chem.*, 68, 266 (1910).

² Travers, A., and Chu, Y. K., *Helv. Chim. Acta*, 16, 913 (1933).

³ Fuchs, N., *J. Russ. Phys. Chem. Soc.*, 61, 1035 (1929).

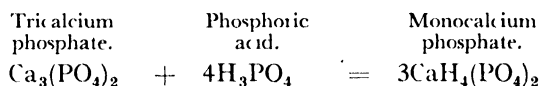
superphosphate: for a small production the material can be dried in drying ovens, and this is economical if waste heat is available. For larger outputs a suitable rotary dryer is recommended.

Double superphosphate should contain from 42 to 50 per cent of P_2O_5 , soluble in water, and should be in a fine, dry, friable condition. In the manufacture of double superphosphate the loss in mixing and drying is approximately 25 per cent by weight.

Double superphosphate is chiefly used as a fertiliser. It is employed to a small extent in the sugar industry, but for this purpose it must be made from arsenic-free acid. A higher-grade product is usually shipped to the sugar estates. The yield of weak phosphoric acid with ordinary working should be about 93-95 per cent, and the yield of crude phosphoric acid should be of the order of 90 per cent. Better results have been obtained in certain special tests, but very complete extraction of the P_2O_5 in the sludge, and careful avoidance of liquor leakages were necessary.

It is known that the efficiency is, in many cases, below the above figure, but with a well-designed plant, and with careful operation, no difficulty should be experienced in obtaining results approximating the yields mentioned. The loss in evaporation indicated above is of the order of 5-9 per cent, and it should be possible to reduce this to 5 per cent.

The broad reaction involved in the manufacture of double superphosphate may be represented thus:



The reactions between most of the impurities (that is, silica, iron oxide, and aluminium oxide, and calcium fluoride, etc.), of phosphate rock and phosphoric acid are not dissimilar to those occurring when sulphuric acid is employed, except that the corresponding phosphate base is produced, instead of the sulphate. Double superphosphate is very similar to the product obtained by the treatment of phosphate rock with sulphuric acid, although it must be remembered that it is not diluted with gypsum, and hence contains a much higher percentage of P_2O_5 , say 40-44 per cent, as contrasted with the P_2O_5 content of say 16-20 per cent in calcium superphosphate. In view of the fact that double or triple superphosphate contains no calcium sulphate to combine with water to form gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the necessity for drying, to which reference has already been made, is obvious.

Concentrated Superphosphate

Under the above heading Raymond L. Copson,¹ of Chemical Research and Engineering, T.V.A., Wilson Dam, Ala., has epitomised current technique in the manufacture of double superphosphate (in America it is called concentrated superphosphate) in the United States.

"When T.V.A. undertook to develop the manufacture of concentrated superphosphate by the use of electric furnace phosphoric acid, batch mixing was adopted in the plant at Wilson Dam, Ala. Finely ground phosphate rock and phosphoric acid (74 to 78 per cent H_3PO_4) were weighed separately in batches and were mixed in a batch mixer. The product, often called double or triple superphosphate, contained 44 to 48 per cent available P_2O_5 .

"The product was dry enough to be stock-piled within a few minutes after mixing, and neither extended curing nor artificial drying was necessary. However, powerful mixing machines were required and maintenance of the mixers was expensive.

"The batch mixing process as used at T.V.A. was described by Curtis,² who also pointed out the probable advantage of a continuous process and described work on development of such a process.

"When the raw materials described above are mixed rapidly, the mixture remains fluid for about 30 secs., then becomes plastic and changes to a hot, moist solid in a matter of two or three minutes. These changes occur much more rapidly than when sulphuric acid is used. The possibility of accomplishing the mixing during the very short period while the mixture is fluid was studied by Copson, Newton and Lindsay,³ who gave a flow diagram of a continuous mixing process.

¹ *Chem. & Met. Eng.*, May 1945, Vol. 52, 5, p. 218.

² *Chem. & Met. Eng.* Sept. 1935, pp. 488-91.

³ *Ind. Eng. Chem.*, 29, 175, 1937.

"Development since that time has consisted of the adaptation of equipment for automatically controlling the rate of feed of raw materials, simplification of the mixing unit and increase in capacity.

"In the present installation, finely ground phosphate rock is supplied to the mixer by means of a weigh-feeding conveyor unit which automatically regulates the rate and records the amount supplied. The rate of flow of phosphoric acid is controlled automatically by means of a stainless steel rotameter with a magnetic coupling device, a recording controller and a controlled valve. By adjustment of this equipment, the rate of production may be varied from about 15 to 35 tons per hour.

"In the development of a high-speed mixer, difficulty was caused by adherence and solidification of the mixture upon the blades and inner surfaces. By experimentation, a mixer was developed to handle this material satisfactorily.

"From the mixer, the mixture falls on to a moving rubber belt where it quickly sets to a solid mass. The rubber belt conveyor is enclosed in a housing from which fumes are exhausted. After remaining on the belt a few minutes the product falls on to a pan conveyor, then goes to a bucket elevator and is conveyed to storage. It reaches the storage pile in the form of small solid lumps. Recovery from storage, disintegration, screening and bagging are the same operations as with batch-processed material.

"This development has indicated that continuous production of concentrated superphosphate is entirely practicable. In comparison with batch-mixing, the continuous process is characterised by lower costs for labour, power and maintenance, and can be made practically automatic in operation."

It is interesting to record here¹ that Messrs. Fisons, Ltd., announce that they have approved plans which are calculated to make a substantial contribution to the need for increased quantities of fertilisers in the United Kingdom. It is proposed to erect a new factory for the production of 100,000 tons a year of triple superphosphate and other fertilisers. Hitherto triple superphosphate has not been manufactured in this country, though during the war considerable tonnages were imported from abroad.

It is understood that a site of 200 acres has been acquired, alongside the North-Eastern Railway Company's Docks at Immingham, Lincolnshire, which will provide facilities for large ocean-going steamers, together with excellent rail and road connections.

¹ *Fertiliser J.*, April 24, 1946, p. 271.

CHAPTER XIV

TREATMENT OF BONES, AND MANUFACTURE OF BONE SUPERPHOSPHATE

THAT the discovery of the fertilising value of bones cannot be attributed to any one person is generally conceded. Common with all other waste materials of animal origin, trial was made, and their properties appreciated, by many people in all ages and in different countries. The nineteenth century appears to have witnessed a growing demand, due undoubtedly to the impetus that the introduction of machines for reducing bones into small pieces, or powder, created.

About 1815 it was found that the home supply was inadequate, and quantities began to be imported from the Continent in rapidly increasing tonnages, until something approaching 30,000 tons per annum represented the imports. Since that time, up to the twentieth century, importations have fluctuated; trade with the Continent has been a varying one, and India and South America have supplied important and increasing quantities. In 1906 the imports amounted to 42,600 tons, and the production at home was computed to be about 60,000 tons. Although they do not now constitute the primary phosphatic raw material, bones are indeed valuable, as the subjoined tree, Fig. 104A, makes abundantly clear. The importation of bones into this country in 1937 was 27,746 tons for the manufacture of manure, and 9,515 tons for glue-making, and the production at home was estimated to be 20,700 tons in 1935.

Developments recently have been in the direction of using better grades of steamed bone flour as feeding stuffs—hence the quantity of bone superphosphate manufactured has been reduced. Recognition of the high availability of the phosphate (80 per cent citric-soluble) of steamed bone flour has led to the employment of this product as such, rather than its treatment with sulphuric acid.

It is interesting to observe that bone greases are now produced both for edible purposes and the higher grades of toilet soap manufacture. Equally interesting is the fact that bone glue is now largely sold in "pearl" form.

A spectroscopic analysis of calcined commercial bone gave as trace elements—calcium, phosphorus, magnesium, sodium, silica, lead, tin, iron, strontium, and barium. Copper was not sought as copper electrodes were used in the experiment.

Rarely are bones used in their raw condition as received from the collectors. Invariably they are submitted to one or other process of treatment. Before proceeding to a consideration of the treatment processes, it will be appropriate here to say a few words concerning the composition of bones and to give below the derivative products of bones.

Seventy per cent or so of the dry bone consists essentially of calcium phosphate. In addition, after incineration it will be found that the ash contains some lime, and a little undecomposed carbonate of lime.

Interlacing the complete mineral framework is the cartilage, constituted of nitrogenous compounds—collagen, chondro-mucoid, etc. The two last-named substances are insoluble in acids, and remain in a soft, tenacious condition after the bone is soaked for some time in weak acid. Fatty matter is associated with the cartilage. The bones of the young are richer in cartilage than those of the old. On the contrary, it will be found that the old contain some inorganic or mineral matter. Again, fatty matter exists to a greater extent in fully developed animals than in those only partially developed. The amount of fat varies according to the nature of the bones. Thigh and leg bones yield 18-19 per cent. Those of the head, ribs, or shoulder blades may not average more than 10-12 per cent.

Initially, bones may either be steamed, or subjected to a solvent extraction process. If steamed, they undergo treatment in a digester, under a pressure of 15 or 20 lb., in order to melt and remove the fat, which is sold as water-rendered bone fat, or used at once for soap-making. If a more efficient extraction of the fatty matter is desired, then a solvent extraction process is resorted to, employing petroleum ether (benzene), and sold as benzene extracted bone grease or fat.

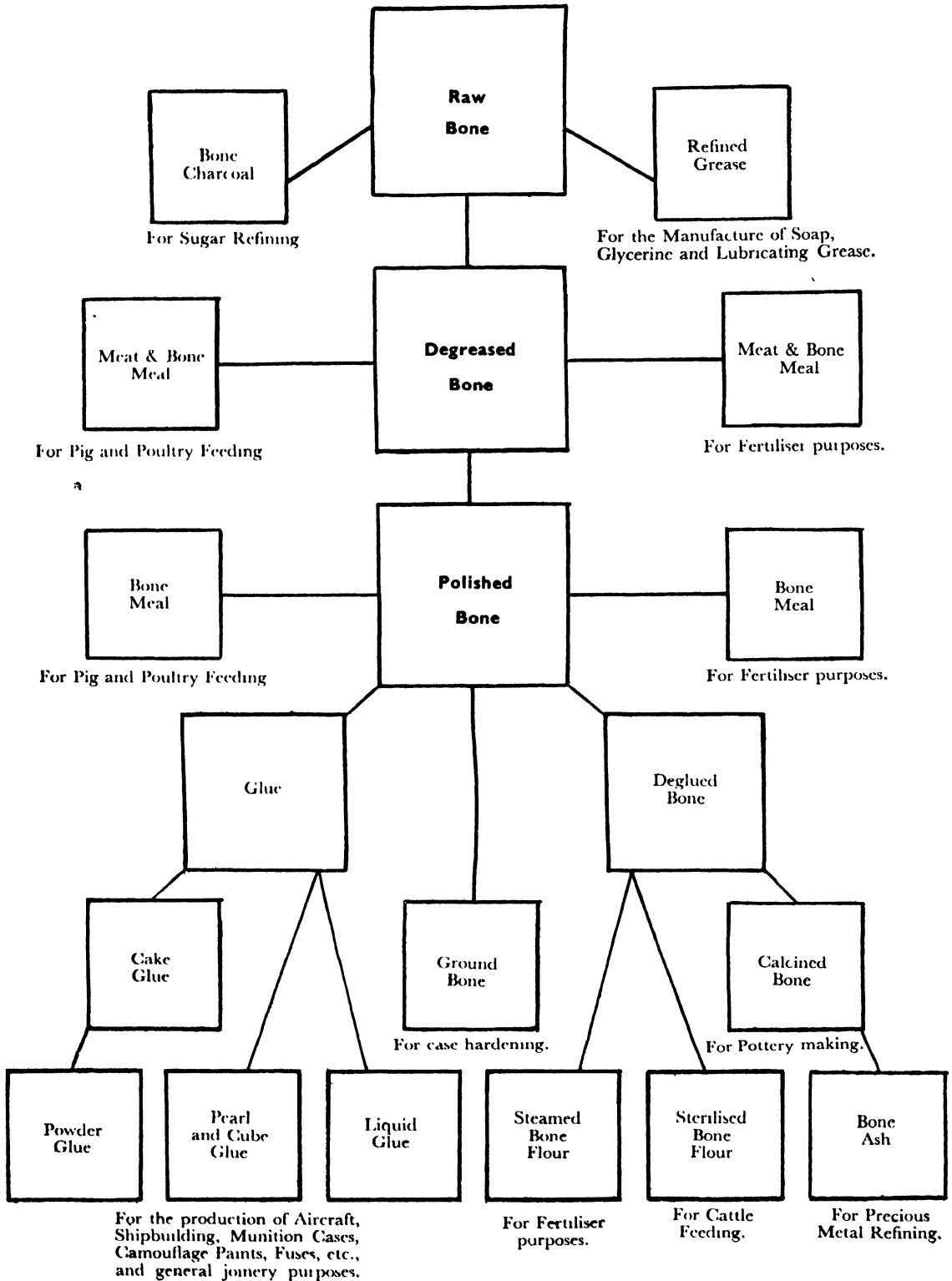


FIG. 104A— DERIVATIVE PRODUCTS OF RAW BONE

It should be remarked here that certain manufacturers, although in a minority, use carbon tetrachloride, known under the trade name of "Westrosol," as an extracting medium. "Westrosol" is very volatile, has a high specific gravity, and can be stored under water, its major advantage being that it is non-inflammable. But its higher price doubtless militates against its use.

A suitable type of plant consists of (1) an extractor, having a capacity of about 10 tons, (2) a still, (3) a condenser, (4) separator, and (5) store tanks for the condensed spirit. The extractor and still are made of best mild steel, and the former is fitted with a perforated false bottom, under which are disposed dry and wet steam coils.

It is important to ensure that the condensers are of adequate size. Design is very important. Not only should there be plenty of surface area for the dissipation of the heat, but a specific turbulence should be given to the water, and the travel of the latter should be such that short-circuiting is obviated.

The raw bones should not be allowed to accumulate for any length of time, otherwise decomposition may set in, with a loss of nitrogenous matter and fat.

Sorting the bones is the first operation. Apart from actual sorting, it is wise to pass the bones over a magnetic separator before passing to the crushers, which break them into pieces 3 or 4 inches long.

Opportunity must be given to the benzine to permeate the whole of the bones. The extracting medium used is an aliphatic, and not an aromatic derivative. In other words, it is not coal-tar benzene, but petroleum benzine, having a well-defined distillation range, which is used.

It is important to select a proper type of solvent, so that a too-rapid or too-slow extraction is avoided, and the steam consumption is of a reasonable order. A specification to which many technicians work is as follows: benzine should boil at approximately 95-100° C., with little or no distillate below that temperature.

The working of the plant is on much the same principle as an ordinary Soxhlet's fat extraction apparatus, with the laboratory use of which many readers will be familiar. Bones can be degreased to such an extent that only 0.50 per cent of fatty matter remains, and the condensing system can be so efficient that not more than say 1.0 per cent of solvent is employed. Bone fat is sold to-day on the basis of 2 per cent of impurities: in other words, containing 98 per cent of fat and quite free from benzine.

Such a fat needs to be refined by further boiling with steam.

The degreased bones, containing approximately 50 per cent of tribasic calcium phosphate and 4.6 per cent of nitrogen, can then be dealt with in three ways: (1) for the manufacture of glue, with steamed bones as a by-product; (2) for the manufacture of pure dissolved bone; and (3) for carbonisation into charcoal, with tarry matter and ammonia as by-products.

There are four classes of products: (a) raw bones, containing the whole of the material, including fat and glue-forming material; (b) bone meal, containing the glue-forming material but not the fat; (c) steamed bone flour, containing the glue-forming material and about 6 per cent of proteins; and (d) dissolved bones, being bones or bone meal treated with sulphuric acid. Typical analyses are furnished in the following table:

TABLE 42

	Nitrogen. Per cent.	Equivalent of ammonia. Per cent.	Phosphoric acid (P ₂ O ₅). Per cent.	Equivalent of tricalcium phosphate. Per cent.
English degreased bones . . .	About 5	About 6	About 22	About 48
Bone meal, usual analysis . . .	3.75	4.5	20.6	45
Steamed bone flour	0.8-1.25	1-1.51	25-32	55-69
Dissolved bones	2.75-3.0	3.3-3.6	14-16	30.6-35

It will be preferable to deal separately with each of the foregoing bone fertilisers.

Raw English Bones

In the crushing of bones it is usual to reduce the size in a crusher initially, and then subsequently to use a Carr's disintegrator, or a Sturtevant hatchet-hammer pulveriser.

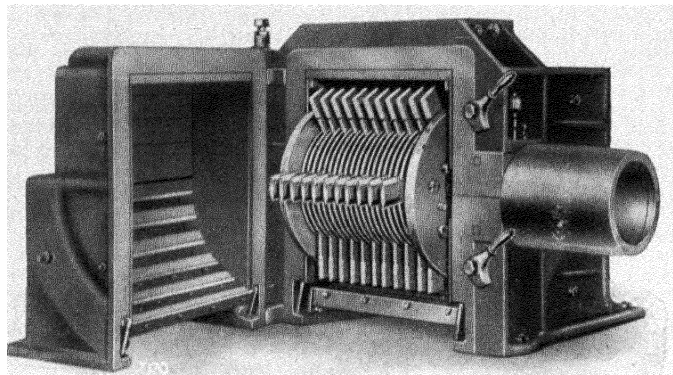


FIG. 105. STURTEVANT HATCHET-HAMMER PULVERISER

The first type of machine is a slow-speed one, consisting of two large rolls formed by thick circular-toothed discs. The teeth are so fixed as to correspond with the circular part of the smaller diameter of the roll. One of the rolls is on movable bearings capable of travelling should the resistance be too great. A set of springs restores the roll to its original position.

If there is no intention of degreasing the bones, which happens very rarely, then the partially crushed bones must be passed to a Carr's disintegrator or a Sturtevant mill. More often than

not the bones will have been degreased, and in some cases partially degelatinised.

Fig. 105 shows the Sturtevant hatchet-hammer pulveriser, equipped with 54 to 66 hammers, rotating at 1,500 revolutions per minute. It strikes from 81,000 to 99,000 hatchet blows per minute, reducing the bone to a very small size.

Fig. 106 shows the layout of a plant as supplied by J. Harrison Carter, Ltd., of Dunstable. In this case the plant consists of an elevator so disposed that the bones can be fed into the boot and made to supply the hopper of a Carr's disintegrator. There the bones are ground to a fine state of division. They are discharged from the disintegrator into the boot of a second elevator, and subsequently fed to the rotary hexagonal reel, having a wire mesh of varying sizes, so as to give different grades of material. Fine material is produced in the first half and medium and coarse in the second half. The tailings are discharged at the end and usually return to the disintegrator again.

To prevent dust, the points at which dust-laden air is likely to arise are connected to a dust balloon.

Bone and other Organic Fertilisers of Animal Origin

It will be appropriate at this juncture if analyses and implied definitions of the above are given.

TABLE 43.

Steamed Bone Flour Meal.

Implied Definition (F. & F. Act). Commercially pure bone from which the nitrogen has been removed by steam.

Average Analysis. Nitrogen 0.82% = Ammonia 1%.
Phosphoric acid 27.5% to 29.75% = Phosphates 60% to 65%.

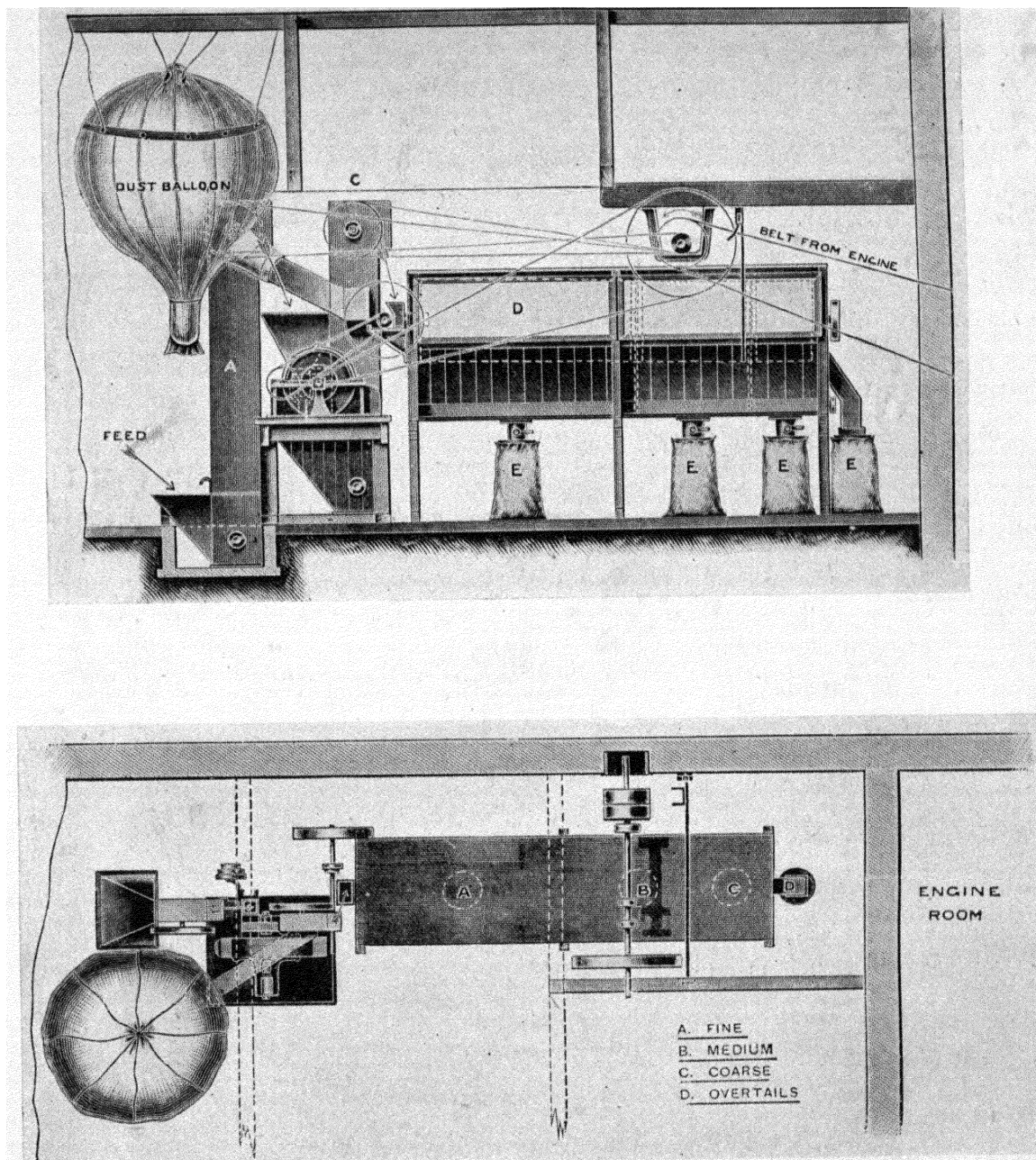


FIG. 106—PLAN (below) AND ELEVATION (top) OF PLANT BY J. HARRISON CARTER LTD. FOR BONE SUPERPHOSPHATE MANUFACTURE.

Full analysis of Steamed Bone Flour (65% Phosphate).

Moisture	12.00
Organic*	10.57
P ₂ O ₅	29.77
CaO	41.16
MgO	0.47
Sulphates and sulphites	0.42
CO ₂ , fluorides and water of hydration	5.10
							99.49

* Containing

Nitrogen	.	.	.	0.79		
Albumenoids	.	.	4.94		Citric solubility	80%

Bone Meal.

Implied Definition (F. & F. Act). Commercially pure bone, raw or degreased, which has been ground or crushed.

Average Analysis. Nitrogen 3.75% = Ammonia 4½%.
Phosphoric acid 20.5% = Phosphates 45%.

Dissolved or Vitriolised Bone.

Implied Definition (F. & F. Act). Commercially pure bone which has been treated with sulphuric acid.

Average analysis. Nitrogen 3% = Ammonia 3.6%.
Phosphoric acid 6.4% = Phosphates 14%
(Water-soluble) (Water-soluble).
Phosphoric acid 8.23% = Phosphates 18%
(Citric and Insoluble) (Citric and Insoluble).

Meat and Bone Meals (Various Grists).

Implied Definition (F. & F. Act). A product of drying and grinding or otherwise breaking bone flesh, flesh fibre (including whale meat), and other slaughter-house residues, to which no other matter has been added.

Average analysis. Nitrogen 4 to 8% = Ammonia 5 to 9%.
Phosphoric acid 9 to 18% = Phosphates 20 to 40%.

Hoof and Horn Meal.

Implied Definition (F. & F. Act). A mixture of hoof and horn crushed or ground to which no other matter has been added.

Average analysis. Nitrogen 12.75% = Ammonia 15.5%.

SUMMARY.

Steamed Bone Flour or Meal grist containing 0.82% nitrogen and 27.5 to 29.75% phosphoric acid and *Bone Meal* containing 3.75% nitrogen and 20.5% phosphoric acid.

These two grades are by far the most extensively used of Bone Fertilisers. *Steamed Bone Flour* (or Meal) is a highly concentrated phosphatic fertiliser, of excellent availability. It mixes well with other fertilisers, and has a definite alkalinity in the soil. *Bone Meal* is an excellent general fertiliser, containing a useful percentage of organic nitrogen.

Dissolved or Vitriolised Bone, containing 3% nitrogen, 6.4% water-soluble phosphoric acid and 8.23% citric and insoluble phosphoric acid (5.49% citric, 2.74% insoluble).

The oldest and original form of water-soluble phosphoric acid, of excellent availability, but has of recent years been largely replaced by the cheap superphosphate produced by dissolving rock phosphate.

Meat and bone Meals, containing 4 to 8% nitrogen and 9 to 18% phosphoric acid.

A very valuable range of organic fertilisers, with usually more nitrogen and less phosphoric acid than bone meal. The tonnages available are, however, distinctly limited.

Hoof and Horn Meal, containing 12.75% nitrogen.

The safest and most stable form of purely nitrogenous fertiliser, giving a steady release over a considerable period. Again, unfortunately, the tonnage available is comparatively small.

Dissolved Bones (Bone Superphosphate)

It has already been observed that the dissolved bones are prepared from bone meal by treatment with sulphuric acid. Broadly, the manufacture of dissolved bones is much the same as that involved in the production of calcium superphosphate by the old processes.

If complete vitriolisation is to be secured, it is necessary that the bones should be in a reasonably fine state of subdivision. Works prefer that the bones should be ground to pass $\frac{1}{8}$ -inch mesh sieve.

The action of the acid on the bone dust takes place rapidly, and the mixing operation is of short duration. The mixture should be transferred to the den without loss of time.

There are not a few problems which arise in the manufacture of dissolved bones. Perplexed by the difficulties attending the rapid mixing and rapid charging, relief is found by some manufacturers in the use of a dilute acid. This reduces the rate of reaction somewhat, but invariably produces a damp and unsatisfactory final product.

Although bones do not contain anything approaching the same amount of fluorine or chlorine as the majority of mineral phosphates, yet objectionable gases are evolved, and precautions need to be taken lest the workmen are affected thereby.

There is not the same effervescence with ground bones as with mineral phosphates, because less carbonic acid is released. It is well to get accustomed to the use of a fairly strong acid with rapid mixing and charging. In this way a consistently good bone superphosphate can be removed from the dens. If a reasonably dry product is required the heat of reaction should be conserved, and the passage of heated air through the material may constitute a wise precaution.

If manufacturers use a weak acid the excess water must be removed in some way or another. Usually artificial drying has to be resorted to, with the result that there is reversion of some of the water-soluble phosphate.

At some works, in order to overcome the bad conditions attending the preparation of bone superphosphate, it is the practice to mix some mineral phosphate along with the bone meal. Thus at one works it has been the practice for some time to mix

6 cwt. of bone meal, containing¹ 3 per cent of ammonia (NH₃)
and 45 per cent of tricalcium phosphate ;
3 cwt. of mineral phosphate ; and 5 cwt. of 125° Tw. acid.

A final product of satisfactory quality is obtained by using the above mixing, but such product must not be described as pure dissolved bone, but as dissolved bone compound.

¹ Bone meal usually contains $4\frac{1}{2}$ per cent ammonia and 45 per cent total phosphates.

Many manufacturers, who are accustomed to mix in the mixers attached to mechanical dens, use their plant for the preparation of bone superphosphate. The method adopted in the case of the Sturtevant den is to remove the door, and as the mixings are from time to time deposited in the den the conical heap is broken down and levelled off. This has been found to be a satisfactory method.

The finished product represents approximately 30 per cent increase of weight on the bone meal used, when the latter is exclusively the raw material.

The following is a mixing and analysis of a pure vitriolised bone fertiliser :

<i>Mixing</i>	
Bone meal	70 per cent
Bone flour	8 "
Sulphuric acid 100° Tw.	27 "
	<hr style="width: 10%; margin-left: auto; margin-right: 0;"/>
	105
Loss	5
	<hr style="width: 10%; margin-left: auto; margin-right: 0;"/>
	100
	<hr style="width: 10%; margin-left: auto; margin-right: 0;"/>

The guaranteed analysis of the above fertiliser is :

Ammonia	3.25 per cent
Phosphates	32.00 " of which
	12 per cent is water-soluble.

The actual analysis is :

Ammonia	3.46 per cent
Total phosphate	33.39 " of which
	15.54 per cent is water-soluble.

Plant for the Manufacture of Bone Superphosphate

Fig. 107 shows an arrangement of grinding and mixing plant, with a section of the dens, mixers, acid weigher, and bone weighers, etc. Fig. 108 shows the bone vitriolisation plant. A few details concerning the basis of the design of this plant are bound to be of interest to our readers. The plant is one designed by the authors for erection in India for the treatment of jungle bones. It comprises a swing sledge-hammer mill having a $\frac{1}{8}$ -inch grating, to give a product capable of passing a 12-mesh sieve. The whole of the ground material is passed to a Newaygo screen fixed at an angle of 45°. The tailings resulting are recirculated.

Subsequently the screened bone meal is passed to a storage bin and elevated as required to the bone weigher and introduced to the mixer degree by degree, after the requisite quantity of acid has been weighed and added to the mixer.

The bone superphosphate is discharged to the conical wooden dens, which are so arranged and disposed that they can be displaced by mechanical dens whenever the time is considered opportune.

The plant in question is capable of producing in ten hours 30 tons of bone superphosphate corresponding to about 20 tons of bone meal. As the capacity of the swing sledge mill is approximately 10 to 15 cwt. per hour, or (say) 15 tons per day, it is clear that two mills are required, and that these should be operated for twenty-four hours per day.

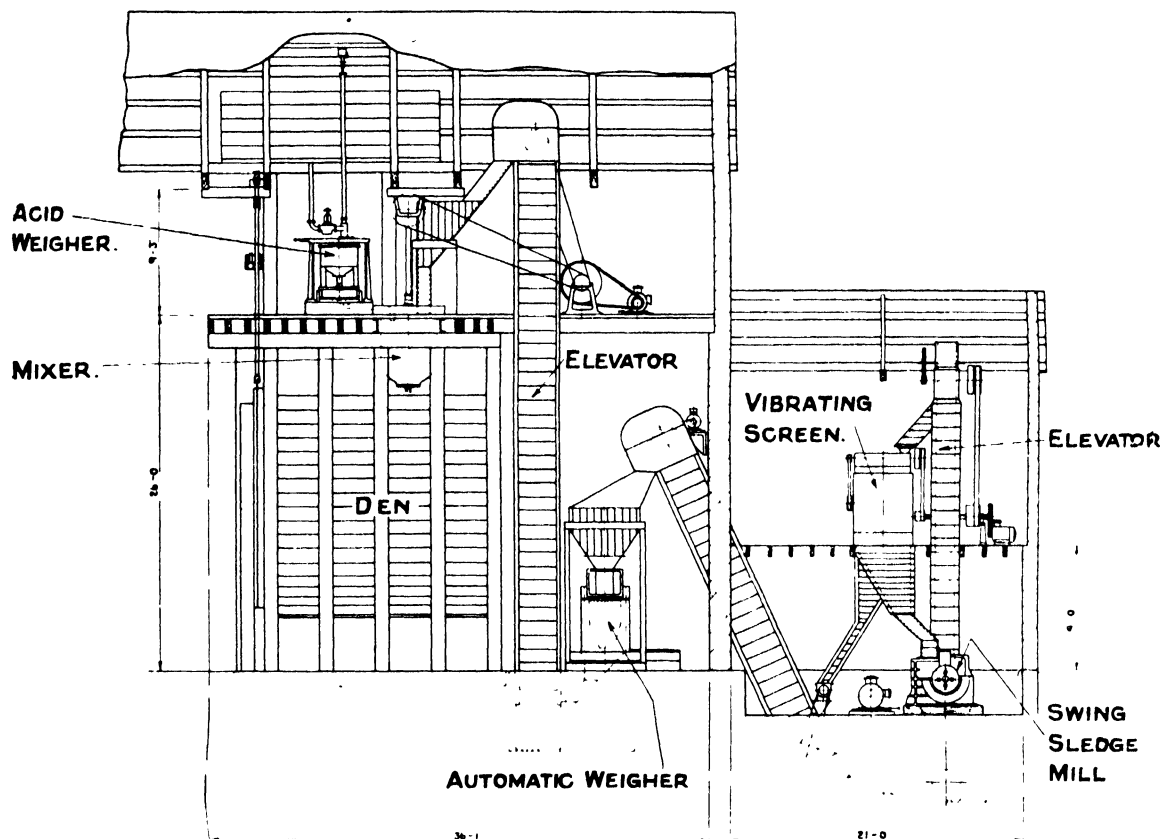


FIG. 107.—BONE SUPERPHOSPHATE GRINDING AND MIXING PLANT

Bone and Potash Fertilisers

Potassic Bone Flour is a mechanically produced mixture of English steamed bone flour and potash (guaranteed to contain no other additions). Such a fertiliser is designed to supply bone phosphates and potash in suitable proportions for general purposes, simultaneously affording economies of time and labour in handling and application.

Analysis : Ammonia	0.5 per cent
Potash (as K_2O)	7.0 "
Bone phosphates	30.0 "
=Insoluble phosphoric acid	13.75 "

In a similar manner, excepting for the addition of water-soluble phosphate to make it somewhat more rapid in action, and suitable for spring application, *Potassic Bone Superphosphate* of the following analysis is a product available on the market.

Analysis : Ammonia	0.5 per cent
Potash (as K_2O)	7.0 "
Water-soluble phosphates	6.0 "
=Soluble phosphoric acid	2.75 "
Bone phosphates	27.0 "
=Insoluble phosphoric acid	12.35 "

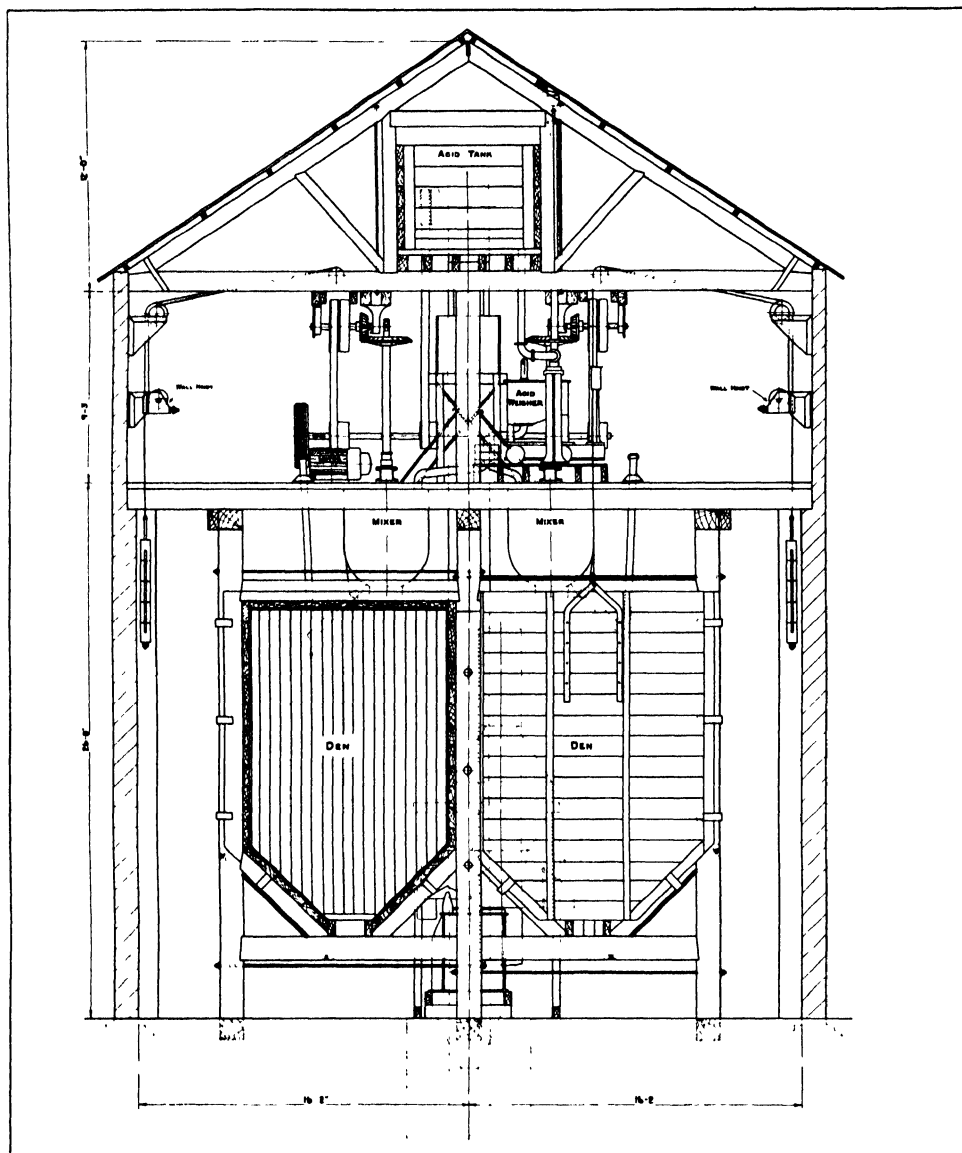


FIG. 108.—BONE VITRIOLISATION PLANT

Potassic Meat Meal and Bone Meal.—By the addition of muriate or sulphate of potash to a high-grade degreased meat and bone meal, a satisfactory base fertiliser is manufactured. It contains the requisite plant foods in available but stable form: it is said to give results not less satisfactory than those of a complete and balanced fertiliser.

Analysis : Ammonia	7.0 per cent
= Nitrogen	5.75 "
Potash (as K_2O)	5.0 "
Phosphate of lime	27.0 "
= Phosphoric acid	12.36 "

There is something significant in what was remarked by Sir Daniel Hall many years ago, that "steamed bone flour does not receive the credit it deserves." No one will doubt the practical worth of organic material: but it would be interesting to know how steamed bone flour compares with calcium superphosphate and basic slag.

Adequate organic matter is an essential accompaniment of high fertility. The continual breaking-down of organic matter in the soil demands constant renewal. The influence of organic matter on soil fertility has been represented in some such terms as the following:

- (a) It provides the plant with a supply of combined nitrogen and other fertilising elements.
- (b) It exerts a beneficial effect on the tilth, moisture-retaining capacity, and temperature of the soil.
- (c) It influences the general soil reaction by the liberation of weak organic acids for combination with soil bases, and
- (d) It provides a habitat, as indeed nutriment, for useful soil micro-organisms.

Guano.—Guanos are not used to any great extent in Great Britain, although horticulturalists are often advised to take advantage of them. Guanos having an appreciable content of P_2O_5 rarely contain much nitrogen. A guano containing little nitrogen usually merely consists of organic matter of no great importance. The phosphoric acid in guano is present as $Ca_3P_2O_8$ and it must be treated with sulphuric acid to render it available. Guano so treated is termed dissolved guano and the water-soluble P_2O_5 is similar to that of calcium superphosphate.

Fish, Fish Meal and Fish Manures

The recent acute shortage of food has brought into prominence the question of fish as a food, as a feeding stuff and as a fertiliser. When several trawlers arrive together, as happens, one cannot deal with all the fish which they bring. As much as possible is sold as food, but quantities are disposed of to the fish manure works, which also deal regularly with the offal from the dressing of fish. Some factories deal with a thousand tons of fish per day in the production of fish meals, fish oils, etc.

Fish contains 75 to 80 per cent of water. In the treatment of 1,000 tons of fish per day, one recovers only about 160 to 200 tons of final product. First-grade fish meal demands best fish. No smell of fish should be transmitted to the cattle and poultry which feeds on it. The oil content of white fish is negligible, but from herrings, mackerel, brisling, sardines and the livers of fish, oil is extracted.

Compound Fish Manures.—Analyses range from 2.5 to 6.0 per cent nitrogen, 3.66 to 9.0 per cent soluble P_2O_5 , 0.88 to 1.42 per cent insoluble P_2O_5 and 0.5 to 7.5 per cent K_2O .

Nota Bene.—If ammonium sulphate or other nitrogenous product is added to bone superphosphate to give an increased becomes content, such a fertiliser, according to the Fertiliser and Feeding Stuff Act, ceases to be dissolved bones, and nitrogen automatically *dissolved bone compound*, the units of nitrogen and phosphoric acid of which are charged at a lower price than in pure dissolved bones.

CHAPTER XV

MANUFACTURE OF BASIC SLAG

THE late Government's agricultural policy was well known. Notable amongst its proposals was the decision to subsidise the purchase of lime and basic slag. It has been suggested¹ that fertiliser manufacturers must welcome the prospect of opening up soils, their sweetening and lightening, and their improvement, by which the application of fertilisers may be of greater usefulness.

Farmers are gratified to be able to obtain basic slag at 25 per cent discount: but fertiliser manufacturers are not so happy. They feel that an undue preference has been given, and that sales of calcium superphosphate may be adversely affected in consequence. Mr. W. S. Morrison (then Minister of Agriculture and Fisheries), said that in subsidising the purchase of lime and basic slag he was thinking in terms of long-range policy, and no less of utilising materials for restoring fertility which are immediately to hand. He would prefer to be independent of any fertiliser which derives from an imported raw material.

Whatever may be the merits of such a policy, and however much fertiliser manufacturers may be affronted, the fact remains that the sale, and incidentally the manufacture, of basic slag have been given a fillip far in excess of what would have been possible by any intensive propaganda. Moreover, the Ministry of Agriculture has published a sectional volume, No. 8, in which users are reminded that "as an effective agent in the improvement of much poor grassland, the use of basic slag merits great attention. The improved effect is to be measured not only by immediate results, such as an increase of herbage, or of meat, or milk, but also by a marked increase in the fertility of the soil, lasting over a period of years."

It was felt desirable to preface this chapter with the foregoing information, as an indication of the importance which one must attach at the present time to the manufacture of basic slag.

For some years the manufacture of steel of suitable quality depended upon the use of ores which were free, or practically free, from phosphorus. As small a quantity as 0.2 per cent of phosphorus suffices to impart the property of brittleness to iron in the cold. As the supply of these ores became depleted, naturally attention was directed by metallurgists to the utilisation of other ores containing a higher percentage of phosphorus, in the hope that these could be successfully taken advantage of.

All the iron ores named, notably those which occur in the Cleveland district of Yorkshire, contain appreciable quantities of phosphorus. In the process of smelting in the ordinary blast furnace a not inconsiderable portion is taken up by the iron. The conversion of cast-iron to steel is inexpensively effected by the Bessemer process, by which (a) air is blown through the molten cast-iron until all the carbon and silicon are oxidised and released, or can be removed; and (b) just enough of an iron, rich in carbon, is added to restore the proportion of carbon and iron which forms the steel. The iron produced in the Middlesbrough area suffered certain disabilities, due to the presence of phosphorus arising from the use of Cleveland ores.

After much research, two chemists—Thomas and Gilchrist—invented a process by which phosphorus could be removed from the material arising in the Bessemer process, and a phosphorus-free steel could be produced from impure Middlesbrough irons.

What is now generally called the Gilchrist-Thomas process consists in lining the "converter," i.e. the large vessel containing the molten iron, with a basic lining composed of lime and magnesia, as compared with the acid lining of bricks largely constituted of silica hitherto used. A large quantity of lime is added and the blast applied. The impurities in the iron at the high temperature which is attained are oxidised by the air introduced. The phosphorus is converted to phosphorus pentoxide, and combines with the lime. A slag is formed containing about 40-50 per cent of lime, with varying quantities of magnesia, alumina, iron oxide, manganese oxide, silica, and phosphoric acid, corresponding to 20-50 per cent of tricalcium phosphate.

¹ *Fertiliser, Feeding Stuffs and Farm Supplies Journal*, June 30, 1937, p. 357.

The process of Gilchrist and Thomas was not applied to any large extent immediately following the discovery. Its introduction was gradual, and some five or six years elapsed before anything approaching universal confidence was reposed in the patented method.

Not only was it used to an important extent in Great Britain, but it was widely adopted on the Continent. The process serves a double purpose. Apart from admitting of the production of an excellent steel, free from phosphorus, it yields a secondary product—basic slag, which has proved a fertilising material of no small importance.

An interesting article bearing on the constitution of basic slag has been published by T. P. Colclough, M.Sc., B.Met.¹ In the article it is explained that in the making of steel by the open-hearth process, the elimination of the impurities in the metal is essentially the result of reactions between the impurities and the slag floating on the surface of the molten metal. The steel-maker controls the operations mainly by the appearance of the slag, which is the only portion of the bath visible to the melter.

The essential constituents of a basic slag are silicon—from the ore or limestone used in the oxidation of the silicon of the metal; oxides of manganese and phosphorus—from the oxidation of these elements from the bath; oxides of iron—from the ore used; and lime, magnesia, and alumina—from the dolomite bed or limestone additions. Colclough deals with the part which silicon, phosphorus, magnesia, manganese, oxides of iron, and spar slags play. It is unnecessary to traverse his observations in detail, as he treats the subject from the point of view of the control of the operations of the steel-maker.

A common practice for some time was to add fluor-spar (CaF_2) to aid the process of desulphurisation, but Colclough makes it clear that its specific purpose has not been rightly appreciated. That a slag containing spar and high lime would remove sulphur from the metal, he concedes as having been well established, but its *modus operandi*, he suggests, is still a matter of speculation.

The first effect of the addition of spar is that the melting-point is lowered, the slag becomes more fluid, and the lime must be fed to prevent attack of the dolomite banks of the furnace. In this way a slag of the same consistency at the same temperature will carry 46-48 per cent CaO with spar, as contrasted with 38-40 per cent CaO in a non-spar slag.

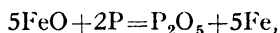
Recent figures² show that such a slag carries its manganese oxide (MnO) in the uncombined state. Reduction of the MnO begins, and manganese is added to the metal.

The use of spar has an important economic effect which should be noted. By reason of its high phosphoric acid content, basic slag possesses valuable fertilising properties, especially for poor grass and root crops. To this (an essential) aspect of the subject with which it is proposed to deal, reference will be made later. What it is desired to emphasise at this juncture is that slags made without the use of spar show a high "solubility" factor, being sold with a guarantee of 80 per cent minimum solubility. Slags made by the processes where fluor-spar is used show very low solubility factors, indeed, as low as 10 per cent, the commercial value of which is almost negligible.

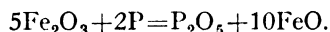
It is pointed out that the work of Scott and M'Arthur demonstrates that this is due to the combination of tricalcium phosphate with the fluor-spar during the cooling and crystallisation, to form the mineral fluor-apatite, $\text{CaF}_2 \cdot 3\text{Ca}_3\text{P}_2\text{O}_8$, as distinct from a silico-phosphate formed in non-spar slags. The silico-phosphate is readily soluble in citric acid solution, while the apatite is not dissolved to any extent.

Colclough summarises the part which phosphorus plays in its relation to basis slag in such a peculiarly lucid manner, that one cannot do better than quote his words and include his own graph.

"Phosphorus.—The phosphorus of the metal is readily oxidised to phosphoric oxide by oxide of iron in accordance with the equations:



or



¹ *Chem. Age*, Metallurgical Section, September 6th, 1924, p. 18.

² Colclough, *J.I.S.I.*, 1923, Part I.

"Unfortunately, the P_2O_5 thus formed is as readily reduced by carbon unless it is held in combination with CaO as calcium phosphate. The constitution of this compound is open to

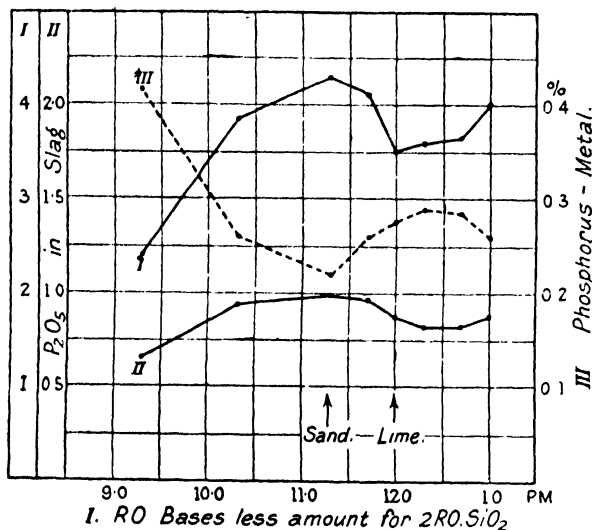


FIG. 109.—CHART SHOWING MOLECULAR PROPORTIONS OF P_2O_5 AND SURPLUS BASES

discussion. It is agreed that it is of the form $xCaO.P_2O_5$, but the differing values of 3, 4, and 5 are given to x by different investigators. The late Dr. Stead firmly established the presence of crystals of tetracalcic phosphate in slowly cooled slag, but in view of the changes which may occur in cooling, this cannot be accepted as final proof of its existence, as such, in the liquid slag. J. E. Fletcher¹ has sought to show that the compound has the formula $5CaO.P_2O_5$, but no experimental evidence is given, and the whole argument is based on the calculations made from the analysis of cold slag. J. H. Whiteley is of opinion that the compound is the tricalcic salt, and in a valuable paper to the Cleveland Institute of Engineers (1922) produces much evidence in support of this. In this paper, however, he assumes the existence of a constituent, a compound of CaO and Al_2O_3 , the reality of which is open to doubt, and his conclusions are therefore not proven.

"In later work² there is given the result of an attempt to determine the equilibrium point between SiO_2 , P_2O_5 , and the bases in the slag, and so to determine the 'critical' basicity of a slag, at which the slag would be saturated with phosphoric oxide. The charge put in the furnace carried a low amount of lime, and the slag at melting corresponded almost exactly to a mixture of $2RO.SiO_2$ with $4CaO.P_2O_5$. Additions of lime and ore were made for two hours, and the oxidation of carbon and phosphorus proceeded simultaneously, there being a slight excess of base in the slag to combine with the oxide of phosphorus as it was formed. At this stage, sand (SiO_2) was added to the slag to reduce its basicity. Immediately a change in the reactions occurred. The oxidation of carbon proceeded normally, but that of phosphorus ceased and was replaced by the reduction of P_2O_5 from the slag—the phosphorus content of the metal rising—i.e. the process as regards phosphorus was reversed and the oxidation of phosphorus resumed.

"Throughout the whole of this period, allowing for time lag due to diffusion and the viscosity of the slag, there is a remarkably close parallel between the molecular proportion of P_2O_5 and the surplus of bases after allowing for the formation of the monosilicate (see chart above) showing that when a slag is saturated with phosphorus the CaO/P_2O_5 ratio is 4/1. This evidence strongly supports Stead's view that the compound formed is tetracalcic phosphate $4CaO.P_2O_5$. This compound is the second essential constituent of a basic slag."

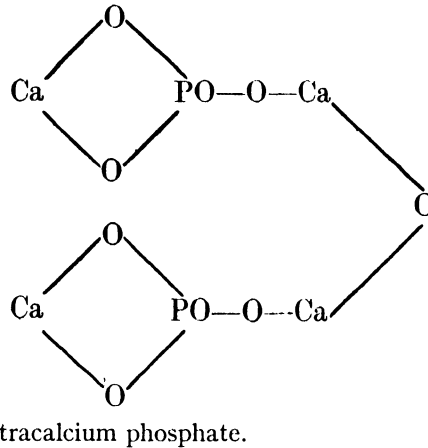
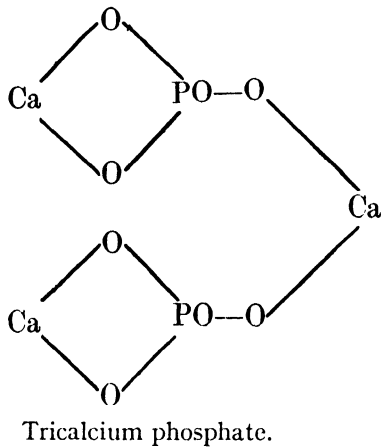
The crude slag is best obtained either as large blocks which have undergone slow cooling in the wagons into which the molten slag is poured, or in large slabs which result from the molten slag being run on to a flat surface.

To aid rapid cooling, it is known that water has been used for quenching, but this practice is attended with considerable risk. A crack may easily develop, and if water reaches the hot internal mass, steam will be formed, with eruptive violence.

¹ Fletcher, *W. of Scot. J. and S. Inst.*, 29, Part VII.

² Colclough, *J.I.S.I.*, 1923, Part I.

In order to elucidate the difference in constitution from the chemical point of view between the normal and the basic salt, the following graphic formulæ are given :—



The following analysis, by Stead and Ribsdale, represents the composition of a typical sample of basic slag produced in 1887 :

	Per cent.
Calcium oxide	41·58
Magnesium oxide	6·14
Aluminium oxide	2·57
Ferric oxide	8·54
Ferrous oxide	13·62
Manganous oxide	3·79
Vanadium oxide	1·29
Silica	7·38
Calcium sulphide	0·54
Sulphur trioxide	0·12
Phosphorus pentoxide	14·36
	99·93

The composition of basic slag varies considerably, and depends, so far as the phosphate content in the final product is concerned, upon the amount of phosphorus in the crude iron, the amount of phosphorus, if any, in the lining, and the extent to which the latter is used. Commercial samples are divided broadly into three grades.

(1) The old Bessemer slag, on which the Cockle Park experiments were conducted. This contains total phosphorus equivalent to 38·42 per cent tricalcium phosphate, with a solubility of 85 per cent by the official citric acid test. To-day this quality of slag is not too common. Certain quantities are produced in this country, and some is imported.

(2) The present-day open-hearth slag of high solubility, containing phosphorus equivalent to 15·35 per cent tricalcium phosphate.

(3) Open-hearth slag, having a total phosphorus content, as first indicated, but with a much lower solubility, according to the official test.

Good basic slag arises at those works where a relatively small proportion of basic lining is used. As with such a lining the phosphorus is not completely removed, the metal is returned to the converter for a second treatment. The resulting slag contains only a small quantity of phosphorus, and is used for the treatment of the next charge. Thus a sort of counter-current process is established.

It should be noted that the Bessemer process has largely been replaced by the Siemens', or open-hearth, method. The open hearth is heated with producer gas, and into it iron ore, for oxidation purposes, and lime are introduced, and the molten pig-iron is poured over them.

From time to time further quantities of lime are added, and, at a later stage, fluor-spar is introduced for the purpose referred to when discussing the work of Colclough.

The duration of the process is longer with the open-hearth method, as the temperature is lower than that which obtains in the Bessemer process. The charge is tipped into a "ladle," which has just sufficient capacity to hold the steel. The slag overflows into a vessel placed below. This is clearly seen in Fig. 110.

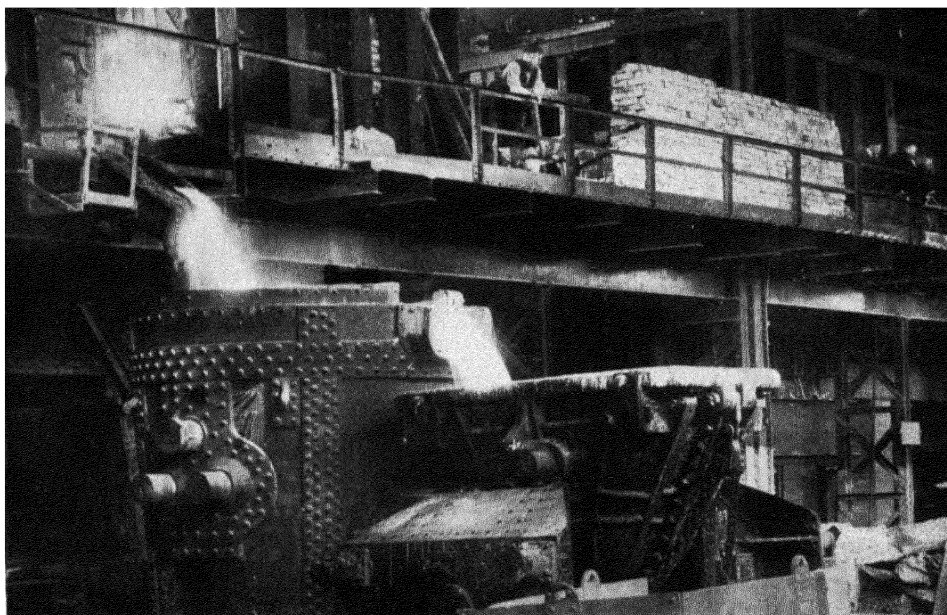


FIG. 110.—MOLTEN STEEL AND BASIC SLAG RUNNING OFF FROM A STEEL FURNACE

Clearly, with each addition of lime, the quantity of slag is increased, with a consequent reduction of its phosphate content.

The solubility of the phosphorus is also affected by the duration of the process, which, as has been indicated already, is increased appreciably. Moreover, the use of fluor-spar tends to produce a slag with low citric solubility. This aspect has been investigated by Professor G. S. Robertson, and was the subject of a paper, "The Influence of Fluor-Spar on the Solubility of Basic Slag in Citric Acid."¹

The grinding of basic slag is dealt with at length in the latter part of this chapter. It is only necessary here to remark that the difficulties experienced in the grinding of basic slag are accentuated by the presence of pieces of steel of various sizes in the slag.

It is known that the finished product may contain many small particles of iron, which are troublesome, because they tend to block the drill, or distributor, when the basic slag is being applied.

It is asserted by some that the fertilising value of basic slag alone depends on the phosphorus which it contains. Others believe that still further research work is needed to determine all the points of value. Originally, Wagner devised a test to extract the basic slag with a solution of ammonium citrate, but later this was altered to a test with citric acid. The purpose underlying the test was the detection of admixed phosphate rock, but for a long time now it has been used as a measure of the solubility of basic slag.

The value of citric solubility determinations appears to be in doubt. Some fertiliser chemists find these indications to be of importance; others regard the results as of little value.

¹ *J.S.C.I.*, 35, 216.

TABLE 44

Complete Analyses of Basic Slag
Average Analysis of Slags Produced

	At Frodingham Iron and Steel Works.		At Dalzell Steel and Iron Works.		By Bolchow Vaughan & Co.		By Dorman Long & Co.		By Park Gate Iron and Steel Works Co.		By Brymbo Steel Co., Ltd.		By Walter Scott, Ltd., Leeds Steel Works.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
Lime	42.90	42.80	44.74	43.24	49.90	36.50	40.00	41.50	45.00	45.00	45.60	42.60	
Magnesia	4.86	5.12	5.04	5.36	7.47	6.34	5.80	4.40	3.60	5.90	5.70	5.70	
Alumina	3.36	1.75	1.86	0.70	2.09	3.33	4.60	3.60	4.10	4.00	4.00	10.95	
Ferric oxide	4.33	6.43	10.28	5.92	5.14	4.43	4.56	6.54	3.10	6.40	10.71	10.71	
Ferrous oxide	10.31	12.98	6.94	10.68	9.13	13.89	9.26	13.27	19.60	8.40	16.00	16.00	
Iron (Fe)	11.02	12.60	14.18	12.46	10.70	13.90	10.30	15.40	16.20	11.00	3.50	3.50	
Manganese oxide	5.58	6.51	7.05	7.98	2.98	2.78	8.67	7.11	5.60	5.60	5.00	5.00	
Silica	17.00	12.40	10.00	10.80	11.70	16.70	10.10	8.80	11.00	10.6	0.45	0.30	
Sulphur	0.21	0.27	0.16	0.15	0.11	0.17	0.07	0.06	0.27	0.45	19.00	19.00	
Phosphoric acid, P ₂ O ₅	9.28	12.71	18.12	13.10	11.00	13.70	14.46	11.26	6.80	12.20	26.60	26.60	
Tricalcic Phosphate of lime	20.23	27.70	23.35	28.59	24.00	29.90	31.55	24.55	14.82	21.47	41.47	41.47	
Citric solubility	80.00	95.00	85.00	70.00	17.50	46.40	86.40	87.50	9.80	0.63	0.63	0.63	

Talbot Furnace Process Metal direct from Blast Furnace.

Talbot Furnace Process Metal direct from Blast Furnace.

Ordinary Open-hearth Process.

Cold Metal Practice.

Hot Metal Practice.

Cleveland Basic.

Open-hearth Slag.

Slagging.

Tap-ping.

Low-grade Slag.

High-grade Slag.

The Ministry of Agriculture and Fisheries, in its leaflet No. 324, points out that it is not quite clear that there is any great difference between the slags of some 60 per cent and others of some 80 per cent solubility, but it does affirm that those of 30 per cent, and still more so those of 20 per cent, solubility are less effective.

The tests on the hay crop at Cockle Park have revealed that the slags of medium solubility are the most useful. Fineness has an important bearing, aiding as it does better distribution, and rendering more easy the solubility of the product after application.

One of the important features of basic slag as contrasted with phosphatic fertilisers is the considerable quantity of lime which the former contains. Lime is valuable for the neutralisation of sulphuric acid which may reach the soil as acid-containing sulphate of ammonia, or may be present as humic and ulmic acids.

With the changes which have been wrought in the processes yielding basic slag as a by-product, by which its composition has been altered, and in view of our present knowledge concerning the solubility of present-day basic slags, the adoption of a better test becomes increasingly insistent. It is understood that data for revision will be available when more field experiments have been undertaken.

In the meantime farmers have been advised to regard the solubility figure as possessing a descriptive rather than a precise value.

Recent analyses of English and continental basic slags are given on page 185. These have been furnished by the courtesy of the Ministry of Agriculture and Fisheries.

TABLE 45
Analyses of Slag undergoing Test at Rothamsted

	A.	B.	C.	D.	E.	F.	G.
Silica	19.35	22.70	19.50	19.50	16.40	19.10	15.40
Manganese	1.96	1.94	1.36	1.38	0.66	6.14	0.89
„ oxide	2.52	2.50	1.75	1.76	0.85	7.92	1.14
Lime	29.80	34.60	38.00	40.50	44.20	30.20	36.40
Iron	4.10	4.80	5.40	5.10	6.60	10.70	3.30
Phosphoric acid	18.59	16.00	15.77	15.48	12.92	18.01	18.47
Citric sol. P ₂ O ₅	15.44	11.10	7.33	6.25	1.40	11.73	4.46
„ solubility	83.07	69.29	46.54	40.37	11.60	75.24	24.14

Slag H.

Total P ₂ O ₅	8.77 per cent
Manganese	8.40 „

Apatite Basic Slag

Slag K

Silica	9.30 per cent
Aluminium oxide	6.32 „
Manganous „	3.25 „
Calcium „	39.50 „
Magnesium „	11.50 „
Phosphoric acid (total)	18.41 „
Total Iron	9.50 „

A, B, C, D, E, F, and G are from Mr. Sillars, of Messrs. Bolchow, Vaughan & Co.; H from Mr. George V. Parker, of The South Wales Basic Slag Co., Ltd.; K from Mr. Bainbridge, of Skinninggrove.

G, of low manganese content, was taken from the same heap as F with high manganese content, but at a later period and after addition of fluor-spar.

B and F are similar in their general analysis and in the amount of their soluble phosphate, but have a wide variation in their manganese content.

TABLE 46

	GERMAN BASIC SLAGS.			FRENCH SLAGS.			Feilitzen and Lugner, 1913.					
	M. Fleischer, 1886 (40 Analyses).			G. Patrel, 1890.								
	Minimum.	Maximum.	Average.	Creuzot.	Hennebont.	Longwy.	Valenciennes.	Swedish.	English.	German.	Belgian.	
Lime	Per cent. 38-00	Per cent. 58-91	Per cent. 49-6	Per cent. 52-00	(1) Per cent. 41-32	(2) Per cent. 43-43	Per cent. 47-70	(1) Per cent. 47-89	Per cent. 49-40	Per cent. 45-64	Per cent. 48-16	
Magnesia	1-14	8-10	4-7	3-01	5-40	7-15	3-74	2-62	3-84	2-19	3-67	
Iron (metallic)	—	—	—	—	—	—	—	1-10	0-29	0-42	0-25	
Ferrous oxide	5-86	18-00	9-3	—	—	—	—	9-35	14-80	7-89	9-56	
Ferric oxide	1-91	7-00	4-1	16-42	15-10	11-25	12-97	9-53	7-44	15-63	6-67	
Alumina	0-14	3-70	2-0	—	—	—	—	8-01	1-06	1-17	1-39	
Manganous oxide	0-55	5-62	4-0	5-79	9-28	6-93	6-97	{ 3-31	4-61	6-61	5-61	
Sulphur	0-05	1-41	0-5	—	—	—	—	0-11	0-07	0-13	0-29	
Sulphuric acid	0-00	1-00	0-2	—	—	—	—	0-10	0-44	0-31	0-14	
Phosphoric acid	11-39	22-97	17-5	14-94	19-20	17-12	18-18	17-01	15-07	18-32	14-55	
Silicic acid	2-70	12-90	7-5	7-84	6-04	7-74	10-44	7-38	6-77	7-61	8-33	
Lime as silicate				7-31	5-63	10-29	9-74					
tetracalcium phosphate				23-56	30-28	30-50	28-68					
free lime				21-13	5-91	2-55	9-28					
				Citric soluble phosphoric acid				15-50	13-05	15-74	13-36	
				Proportion of total slag citric soluble				91-12	86-60	85-64	91-82	
				Lime as free lime				4-90	2-56	3-33	5-05	
				Lime available as base				12-56	9-95	13-19	14-75	
Number of samples analysed				1904.	AUSTRO-GERMAN SLAGS.			1914.	1924.			
Average content of				1587				2242	768			
(a) Total phosphoric acid				Per cent. 17-36	Per cent. 16-66			Per cent. 17-98	Per cent. 17-98			
(b) Citric soluble phosphoric acid				15-36	16-09			16-82	16-82			
				Slags with a total phosphoric acid content of—								
Range of Variation.	Under 16 per cent.	Over 18 per cent.	Under 16 per cent.	Over 16 per cent.	Under 16 per cent.	Over 16-18 per cent.	Under 16-18 per cent.	Over 16-18 per cent.	Under 16 per cent.	Over 16-18 per cent.	Over 18 per cent.	
Number of samples	15	41	7	15	21	5	6	6	6	6	6	
Total phosphoric acid	Per cent. 12-61-15-69	Per cent. 16-05-17-99	Per cent. 10-86-15-98	Per cent. 16-19-17-99	Per cent. 18-16-21-92	Per cent. 15-66-15-86	Per cent. 16-40-17-85	Per cent. 21-26-24-60	Per cent. 16-40-17-85	Per cent. 21-26-24-60	Per cent. 21-26-24-60	
Citric acid solubility	82-98	72-96	80-88	68-95	74-93	89-96	86-98	68-84	86-98	68-84	68-84	
Average total phosphoric acid	14-45	17-07	13-11	17-30	19-71	15-54	17-12	23-08	17-12	23-08	23-08	
citric acid solubility	92	84	85	89	86	94	92	77	92	77	77	

With regard to A to G, it should be noted that although they have all passed through a 90-mesh sieve, the quantity going through a 200-mesh is less than is obtained from ordinary commercial grinding.

Continental basic slag usually gives an analysis of 20 per cent total phosphate (P_2O_5), against Welsh basic slag of 10 per cent total phosphate (P_2O_5). In both cases the solubility in 2 per cent citric acid solution is over 80 per cent. Basic slag is sold on total P_2O_5 with a basis of 80 per cent solubility by the standard 2 per cent citric acid solution, and 80 per cent of the material must pass the standard Amandus Kahl "E" gauge of 10,000 holes to the square inch. An English standard as regards fineness of grinding has now been adopted (see details on page 188).

Table 46 shows typical analyses of German, French, and Austro-German slags.

Lest there be doubt as to what is implied by "solubility" as applied to basic slag, it is well to point out that this figure refers to the part of the phosphate which is soluble in citric acid used in the official test.

By a 20 per cent slag of 20 per cent solubility is meant that in 100 lb. of slag, having a content of 20 per cent of tricalcium phosphate, 20 per cent of this phosphatic material is soluble in the official testing liquid.

The official citric acid test is given below. This has been culled from the Fertilisers and Feed-stuffs (Method of Analysis) Regulation, 1908.

"(1) *Phosphates Soluble in the Prescribed Citric Acid Solution.*—Five grams of the sample shall be transferred to a stoppered bottle of about 1 litre capacity. Ten grams of pure crystallised citric acid shall be dissolved in water, the volume shall be made up to 500 cubic centimetres, and the solution shall be added to the weighed portion of the sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 cubic centimetres of alcohol or methylated spirit before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 cubic centimetres instead of 500 cubic centimetres. The bottle shall be at once fitted into a mechanical shaking apparatus and shall be continuously agitated during 30 minutes. The solution shall then be filtered through a large "folded" filter, the whole of the liquid being poured on the paper at once. If not clear the filtrate shall be again poured through the same paper.

"Fifty cubic centimetres of the filtrate shall be taken, and the phosphoric acid shall be determined by the molybdate method prescribed below.

"(2) *Total Phosphoric Acid.*—A weighed portion of the sample, in which portion, if necessary, the organic matter has been destroyed by ignition and the silica removed by appropriate means, shall be dissolved in nitric acid and boiled, the solution being made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the molybdate method prescribed below.

"(3) *Molybdate Method.*—To the solution, which should preferably contain from 0.1 to 0.2 gram of phosphoric oxide (P_2O_5), obtained as above described in paragraphs (1) or (2), 100 to 150 cubic centimetres of molybdic acid solution prepared as described below, or an excess of such solution, i.e., more than is sufficient to precipitate all the phosphoric oxide present in the solution, shall be added, and the vessel containing the solution shall be placed in a water-bath maintained at 70° C. for 15 minutes, or until the solution has reached 70° C. It shall then be taken out of the bath and allowed to cool, and the solution shall be filtered, the phospho-molybdate precipitate being washed several times by decantation, and finally on the paper with 1 per cent nitric acid solution. The filtrate and washings shall be mixed with more molybdic acid solution and allowed to stand for some time in a warm place in order to ascertain that the whole of the phosphoric oxide has been precipitated.

"The phospho-molybdate precipitate shall be dissolved in cold 2 per cent ammonia solution, prepared as described below, and about 100 cubic centimetres of the ammonia solution shall be used for the solution and washings. Fifteen to twenty cubic centimetres of magnesia

mixture, prepared as described below, or an excess of such mixture, i.e., more than sufficient to precipitate all the phosphoric oxide present, shall then be added drop by drop, with constant stirring. After standing at least two hours with occasional stirring, the precipitate shall be filtered off, washed with 2 per cent ammonia solution, dried, and finally weighed as magnesium pyrophosphate. The filtrate and washings shall be tested by the addition of more magnesia mixture.

“(4) *Preparation of Molybdic Acid Solution.*—The molybdic acid solution shall be prepared as follows :

“One hundred and twenty-five grams of molybdic acid and 100 cubic centimetres of water shall be placed in a litre flask, and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 cubic centimetres of 8 per cent ammonia solution, prepared as described below. Four hundred grams of ammonium nitrate shall be added, the solution shall be made up to the mark with water, and the whole added to 1 litre of nitric acid (sp. gr. 1.19). The solution shall be maintained at about 35° C. for 24 hours and then filtered.

“(5) *Preparation of Magnesia Mixture.*—The magnesia mixture shall be prepared as follows :

“One hundred and ten grams of crystallised magnesium chloride and 140 grams of ammonium chloride shall be dissolved in 1,300 cubic centimetres of water. The solution shall be mixed with 700 cubic centimetres of 8 per cent ammonia solution, and the whole shall be allowed to stand for not less than three days and shall then be filtered.

“(6) *Preparation of the Ammonia Solutions.*—The 8 per cent ammonia solution shall be prepared as follows :

“One volume of ammonia solution of sp. gr. 0.880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution or water as required until the specific gravity of the solution is 0.967.

“The 2 per cent ammonia solution shall be prepared as follows :
“One volume of 8 per cent ammonia solution shall be mixed with three volumes of water.”

Potassic Basic Slag.—At several works basic slag and kainit are ground together in a ball mill, and a most useful mixture, usually having a fineness of 80 per cent through a standard 10,000-hole sieve, is obtained.

The analysis guaranteed is :

Total phosphates	. 30 per cent (24 per cent citric-soluble).
Potash (K ₂ O)	. 5.0 „

There has been considerable controversy regarding the sieves used for determining the fineness of basic slag. The sieve commonly used for determining fineness, when any attempt at a definite standard is quoted, is a German sieve known as the Kahl, and designated 100E.

Another type of sieve has been standardised by the Institute of Mining and Metallurgy of Great Britain, which has this characteristic—that the diameter of the wire and the size of the aperture are identical.

From table 47 it will be seen that a 100-mesh Kahl screen has an opening approximately 18 per cent greater than the I.M.M. 100-mesh screen.

A committee appointed by the Ministry of Agriculture in Great Britain has been considering the possibilities of development and improvement of the manufacture of basic slag and the extension of its use, and in an interim report recently published in the *Journal of the Ministry of Agriculture*,

TABLE 47

	Wire. Mm.	Space. Mm.
Amandus Kahl 100E, Specimen I	0.120	0.143
" " " II	0.110	0.145
" " " III	0.110	0.148
" " " IV	0.126	0.142
Sieve used in German Government Laboratory	0.102	0.150
100 mesh, Institute of Mining and Metallurgy, Great Britain	0.127	0.127
90 mesh, Institute of Mining and Metallurgy, Great Britain	0.141	0.141
80 mesh, Institute of Mining and Metallurgy, Great Britain	0.159	0.159

a specification is drawn up in regard to a standard sieve and method of use for testing the fineness of basic slag. It is as follows :

"(1) The standard sieve for determining the fineness of grinding of basic slag shall be of metal, and circular in shape ; it shall be mounted in a stout circular metal framework ; the parts where the screen meets the framework shall be rounded off by solder, or otherwise, in order to avoid crevices in which powder may collect ; the sieve shall be fitted with a lid and box underneath to collect fine material.

"A convenient size of sieve is one with a diameter of 5 to 8 inches.

"(2) The mesh of the standard sieve shall be of the 'single-weave' type, i.e. each wire shall pass alternately over and under successive wires, and at right angles to those wires.

"(3) The standard sieve shall be of even texture. The standard diameter of the wire and the standard length of side of the aperture shall be each 0.141 mm. No wire shall anywhere be less than 0.138 mm. in diameter, and no aperture shall be greater than 0.155 mm. in length of side.

"(4) The operator shall manipulate the sieve in his own way, providing that no force or pressure of any kind shall be used to persuade particles to pass through the sieve. Sieving shall continue until all obvious signs of material passing through have ceased.¹

"A mechanical shaker may be employed. Soft lumps which can be caused to crumble by the application of the fibres of a bristle brush shall be broken down after each shaking period, but in such manner as to avoid the hard parts of the brush coming in contact with the sieve so as to cause abrasion.

"Sieves will not remain in accordance with paragraph 3 if they are used for other purposes in which either pressure from above is used in the sieving process, or coarse and heavy constituents are present in the material to be sieved."

The prescribed sieve now used for the purpose of the statement as to fineness of grinding of basic slag is a British Standard test sieve, mesh No. 100. The British Standard Specification for Test Sieves, No. 410/1931, is as follows :

Aperture	0.0060 inch—0.152 mm.
Diam. of wire	0.004 ,, —0.102 ,,
Approximate screening area	36 per cent

¹ See note at end of chapter.

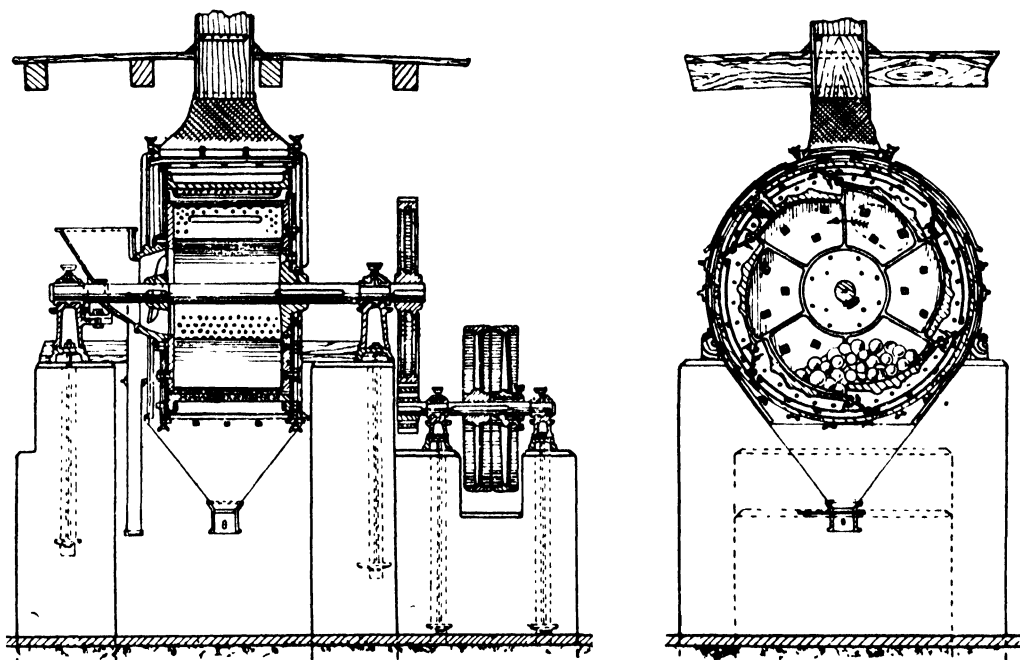


FIG. 111.—KRUPP BALL MILL (SECTIONS)

A suitable apparatus for doing this sieving mechanically is made by Sturtevant, of London and Boston, U.S.A. It is shown in Fig. 115. The test sieves are mounted on top of a vibrating mechanism and held securely in position with a clamping device. The vibrator is coupled direct to a very small electric motor, about $\frac{1}{8}$ h.p., running at approximately 1,200 revolutions per minute. The vibrator operates through an eccentric shaft with about $\frac{1}{16}$ -inch throw. There is a compensating spring on top of the sieves to take up the vibrating force. The sieves are quickly placed in position and removed, and when the mechanism is started no attention is required during the sieving operation. A time-switch can be attached to the mechanism and set to stop the motor at any predetermined period of time.

Such a test sieve can be relied upon for accuracy in sieving and timing, which is practically impossible by hand methods.

Mechanical Aspect

Krupp Ball Mill.—The grinding of basic slag is a difficult problem, and calls for very heavy grinding machinery. The Krupp ball mill was the first machine to be used for the purpose and is still in use to-day. It eliminates the iron from the slag without being seriously damaged. The ball mill retains the lumps of iron, which become grinding media until their accumulation in the mill interferes with the grinding of the slag. Periodically, therefore, the mill has to be stopped and the surplus iron removed.

Fig. 111 shows two sections of a Krupp ball mill. The drum is formed of two circular steel side plates, one of which is secured to a blank and the other to a spider hub. These two hubs, which are made of cast steel, are keyed on to a heavy horizontal shaft at a certain distance apart. Between the two side plates a number of tough cast-steel plates are secured by bolts, the plates being so arranged as to form steps. These grinding plates taper in thickness, and are placed in the mill so that the thick end of one plate overlaps the thin end of the adjacent plate. Several rows of holes are cast in the thin part of these plates: the holes taper from the outer to the inner side.

Around the grinding drum a screen, formed of slotted plates, is arranged, and between the steps of the grinding plates narrow strips of perforated plate are secured, which act as scoops. External to the foregoing there is a further screen, which encircles the mill, and is usually made of phosphor bronze wire cloth, 48 mesh.

The action of the mill is as follows :

The drum is rotated by means of heavy spur gearing, driven through a counter-shaft. The slag is introduced through the spider hub, and is crushed and ground by the falling balls, and, passing through the holes in the grinding plates, falls upon the coarse screens. The slag which is fine enough to pass this falls upon the fine sieve, and that which is sufficiently reduced in size falls through into the sheet-iron hopper casing surrounding the mill. As the drum rotates, the tailings from both the inner and outer screens are returned to the grinding zone by means of the scoop plates.

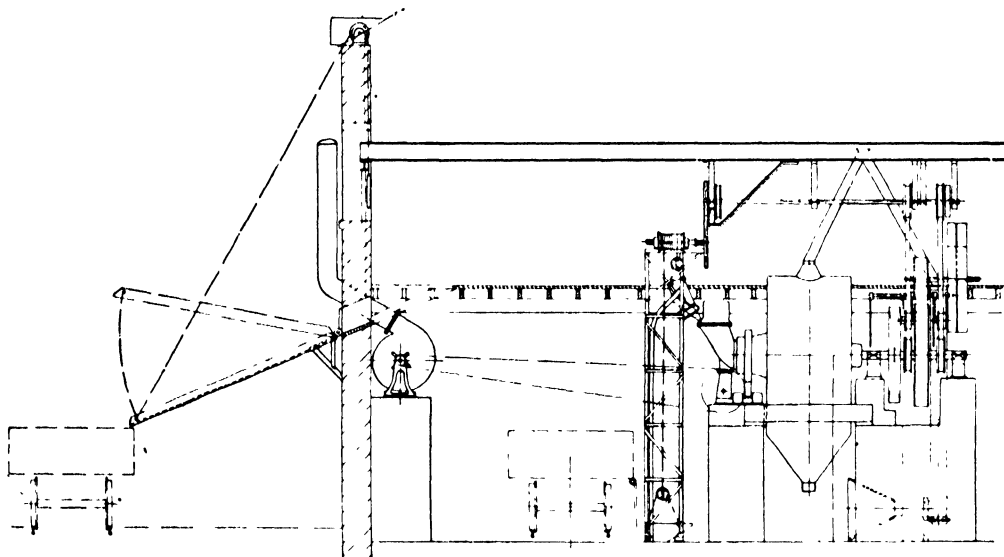


FIG. 112.—ARRANGEMENT OF BASIC SLAG GRINDING PLANT WITH BALL MILL

The balls which are used are made of carbon steel, and are 3-inch, 4-inch, and 5-inch diameter, and as they wear down they are automatically rejected from the mill through a slot-opening in one of the grinding plates. The width of this opening is generally $1\frac{1}{2}$ inches and is fitted with a cover. Periodically the cover is removed and the drum rotated. Balls which have worn below $1\frac{1}{2}$ -inch diameter, and small pieces of iron, fall through the slot-opening into the hopper surrounding the mill. Balls of the largest diameter are then added to the charge in the mill equal to the weight of balls withdrawn.

When ball mills are used for grinding slag to the standard fineness in one operation, the largest size Krupp is generally installed: this is known as No. 8, the drum of which is 8 feet 10 inches diameter by 4 feet 6 inches wide. The total weight of this mill is $15\frac{1}{2}$ tons, including the charge of balls, which weighs 2 tons. The drum rotates at a speed of 20 revolutions per minute.

When grinding slag of average hardness, the capacity of a No. 8 mill is approximately 40 to 50 cwt. per hour, when the moisture does not exceed 2 per cent. The power required for driving is 85 b.h.p., or 34 to 42 b.h.p. per ton per hour. If the slag is damp the output may fall to 25 cwt. per hour. A charge of balls will grind approximately 14,000 tons of slag.

These mills are usually erected at such a height that the bagging can be effected at the ground level. Owing to their immense size, the feed-opening is then about 14 feet above the ground, and mechanical means have to be employed for lifting the slag to the hopper. The most suitable apparatus is a skip-bucket elevator, operated by a friction hoist.

A slag plant incorporating one of these skip buckets is shown in Fig. 112. The skip bucket is filled by hand-shovelling at the floor level, and generally holds 5 to 10 cwt. When full, the operator pulls a rope which throws the friction hoist into gear, and the bucket is pulled up by a wire rope. On reaching the top, the track is so arranged that the bucket tips, and its contents are automatically delivered to the mill. The bucket is then lowered by gravity, and is controlled in its descent by a brake drum on the friction hoist.

The plant illustrated in Fig. 112 is equipped with a dust-collecting system. Suction pipes are connected to the top of the mill casing, and to a hood situated near the bagging spout. The dust-laden air is drawn off by means of a fan through an automatic filter, where the dust is arrested and collected in a hopper.

Tube Mill Grinding.—Another system of grinding basic slag employs ball mills and tube mills. At one time these were separate mills, the ball mill acted as a preliminary grinder and delivered the slag in a semi-finished condition to the tube mill, in some cases 10, 16, or 18 mesh.

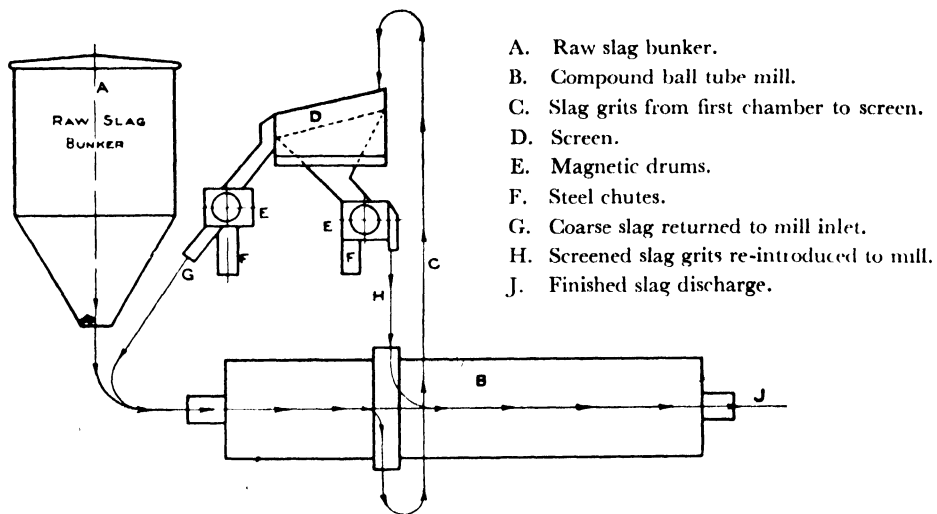


FIG. 113.—FLOW SHEET OF NEWELL'S SYSTEM OF BASIC SLAG GRINDING PLANT

These two mills are now combined in one, and recent plants installed, such as that at Corby, embody a combined ball and tube mill in one machine. They are of immense size and have a capacity of 20 tons per hour when fed with $\frac{3}{4}$ -inch material and grinding to a fineness of 90 per cent through 100 mesh. It will be realised that it would take five or six No. 8 ball mills to do the equivalent work and much more space and handling equipment would be required.

The diagram Fig. 113 shows the flow sheet of the Newell system.

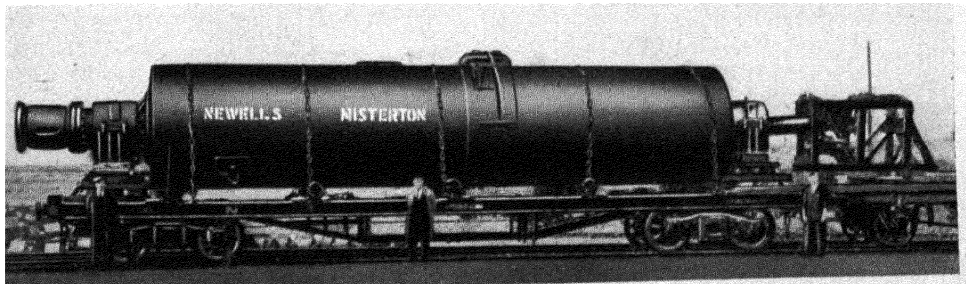


FIG. 114.—NEWELL'S TUBE MILL FOR BASIC SLAG

The tube mill possesses a special feature namely, there are two chambers. The coarse slag grits are taken out of the mill at the end of the first grinding chamber and passed over an electro magnet which extracts the steel and the slag is re-introduced into the second chamber, at the same place, for final grinding. The flow sheet shows a screen in addition to two magnets, which separates out slag above a certain size, and this portion is refered to the first chamber. The illustration in Fig. 114 shows one of these large tube mills loaded on a railway bogey. It is 7 feet 6 inches diameter by 36 feet long. The mill, when rotating at 20.8 revs. per min., requires 450 h.p. to drive it, and to overcome the inertia at starting a 700 h.p. motor is installed.

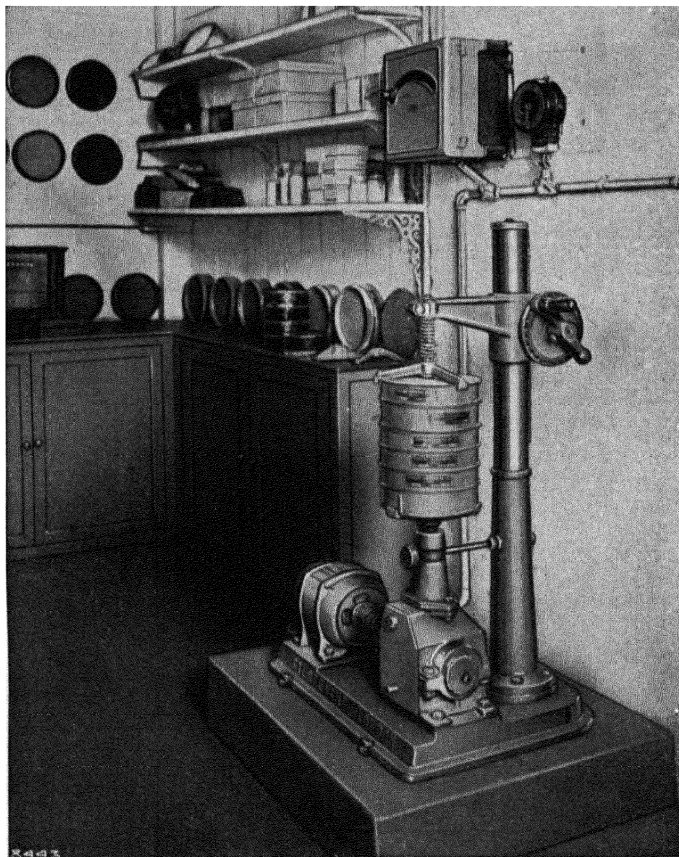


Fig. 115.—STURTEVANT LABORATORY TEST SIEVE

NOTE.—It is suggested that a convenient procedure is to take 20 grams of basic slag and transfer to the sieve with the lower receiver attached. After shaking for ten minutes, with occasional tapping of the sides of the sieve, all the fine material which has passed through into the lower box to be carefully brushed out into a suitable vessel and weighed. The shaking to be repeated for another ten minutes and the sifted matter again removed, mixed with the first portion and weighed. The process to be repeated until not more than 0.2 per cent is sifted during ten minutes.

CHAPTER XVI

MECHANICAL HANDLING OF RAW MATERIALS AND PRODUCTS : CONVEYING PLANT

IN fertiliser works, the transportation of raw materials and finished products at the different stages of manufacture presents a number of problems, and the cost of manufacturing is largely dependent upon a satisfactory solution of these problems.

In works of small size, where the output does not exceed say 10,000 tons per annum, primitive methods are still employed: the navvy barrow is usually the only form of conveyer used.

Before installing modern mechanical handling equipment, one has to consider whether full use can be made of it to justify the initial outlay. In works of the above-mentioned capacity this is often doubtful, particularly owing to the usual scattered arrangement of the buildings and low head room.

In considering the capital outlay of any scheme, the saving in point of manual labour should first be determined. In chemical works, the annual charge for depreciation and maintenance of this class of plant is generally assessed at 10 to 12 per cent. Taking a man's wages at £3 per week, or £156 per year, and capitalising this sum on the 12 per cent basis, the capital equivalent in plant of one man is £1,300. So that if the cost of the scheme divided by the number of men saved is greater than £1,300, there is no financial advantage; on the other hand, if it is less than £1,300, it then shows a saving. For instance, suppose by spending £3,000 on mechanical equipment the

labour of three men can be saved $\frac{3,000}{3} = £1,000$ —the scheme would be a financial advantage;

but if the labour of only two men can be saved $\frac{3,000}{2} = £1,500$ —then it would not be a financial advantage.

In *Chemical Engineering and the Works Chemist* of February, 1921, C. J. Goodwin, B.Sc., A.M.Inst.C.E., contributed an article on conveyors, and arrived at a slightly lower figure of "capital equivalent" in a different way.

He says: "Assume, for example, that the local rate of pay is £3 per week, or £156 per year, and it is proposed to write off the cost of the machine in five years. Five years' wages represent £780, and we will assume that £600 only in capital need be raised by way of a loan. Table 48 shows the way in which the loan is repaid, the total paid out being £780.

"During these five years, the average annual outlay, exclusive of running expenses, is the same as that formerly paid in wages, but at the end of the period the machine, somewhat depreciated, is still available for a further period of usefulness. It may therefore be said that, under normal circumstances, a capital expenditure of £700 to £1,000 is economically justified on a handling installation which dispenses with the services of one man.

TABLE 48

	Capital owing.	Annual amount redeemed.	5 per cent. interest. 15 per cent. depreciation.	Total paid.
1st year . . .	£ 600	£ 120	£ 60	£ 180
2nd „ . . .	480	120	48	168
3rd „ . . .	360	120	36	156
4th „ . . .	240	120	24	144
5th „ . . .	120	120	12	132
				780

A machine like this entails less capital outlay than the installation of a system of conveyors for a like purpose, and it may be used for other purposes as occasion arises.

Another mechanical device for reclaiming the raw phosphate rock from the store is shown in Fig. 118. It consists of a drag line scraper manipulated from a central cabin by means of a winch and wire ropes. The scraper consists of a "Crescent" bucket fitted with hauling and draw-back ropes. These pass through a head post situated at the centre of one side of the store above an underground hopper. The draw-back rope passes through a travelling pulley block attached to rope running round all four sides of the building. From his elevated position, the operator can direct the scraper to any point in the store, as desired.

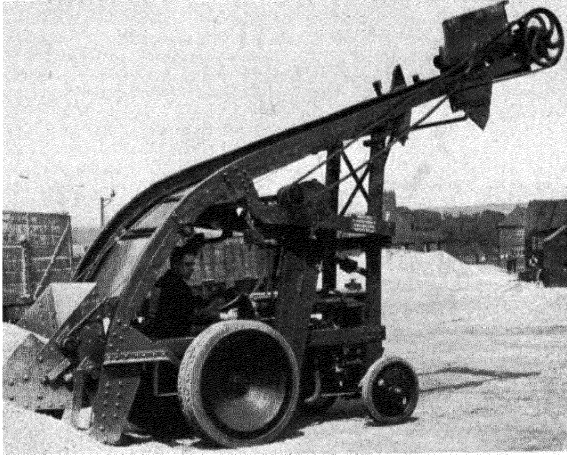


FIG. 117.—ECLIPSE AUTOMATIC LOADING SHOVEL

In Fig. 118 it is interesting to note the design of the phosphate store, which represents the one at the National Fertiliser Works, Avonmouth.

The roof is designed to remove practically all stresses from the side walls and internally is a very pleasing building. It is 300 feet long, 114 feet wide, and 50 feet to the apex, and has a capacity of 20,000 tons of rock phosphate.

Monorails.—Monorail systems are extensively used in fertiliser works, both for conveying the phosphate rock and the superphosphate. The overhead monorail has the advantage that it presents little or no obstruction to ground or surface traffic. Irregularity of floor level does not affect it, and the floor is free from rail-tracks and turn-tables. The track can be arranged at such a level that a man can push the skips along, and as the trolley is generally equipped with two wheels, they run more easily than four-wheeled trucks, as the friction is considerably reduced.



FIG. 118.—DRAG LINE SCRAPER

"The running expenses of the machine in such cases are not appreciably greater than the cost of supervising labour."

For bulk conveyors we think the above figure is rather low, and considering all the conditions under which mechanical equipment has to operate in a fertiliser factory, £1,300 is a more reliable figure upon which to base calculations.

There are two systems of elevating and conveying, which might be termed the "intermittent" and "continuous."

In the intermittent system the material is carried in relatively large units at long intervals, and in the continuous system it is conveyed in small units at frequent intervals, approximating to a continuous stream.

The earliest example of the intermittent system is the navy barrow, succeeded by the side-tipping wagon, and later by the electric truck, mechanical ropeway, electric telfer, and, for large plants, the travelling crane with grab bucket.

The use of barrows for the conveying of materials is not only slow but costly, as the labour entailed is heavy, owing to the man having to support, partially, the load. The tipping truck, running on narrow-gauge rails, is superior in every way, even when hand-propelled, as the man has only to overcome the frictional load, and can easily move a truck containing $\frac{1}{2}$ ton of material.

Side-tipping wagons are largely used in English works for bringing the rock phosphate from the store to the grinding plant; the loading is generally undertaken by manual labour, although in some instances Jeffrey loaders are used. In some large works the trucks are filled by means of navy excavators, or travelling cranes with grab buckets.

The type of truck most commonly used is fitted with roller bearings for easy running, and their short wheel base enables them to negotiate sharp curves.

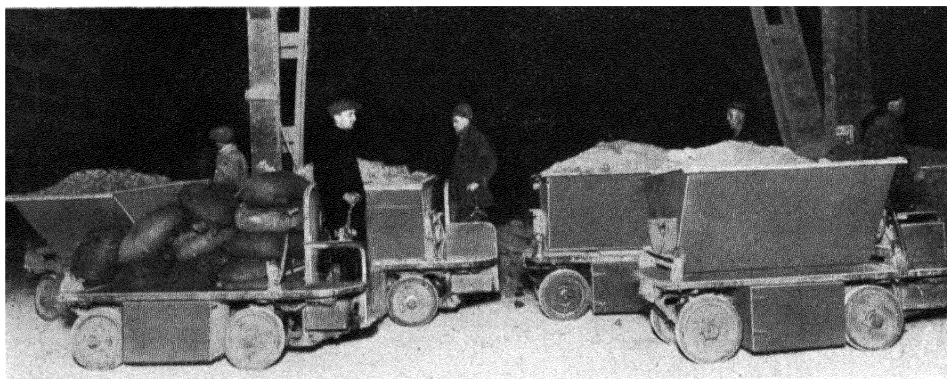


FIG. 116.—STORAGE BATTERY TRUCKS

The latest type of truck is electrically propelled, and is equipped with storage batteries. A group of these is shown in Fig. 116. Storage battery trucks have reduced the cost of handling in some works by as much as 50 per cent. They travel at the rate of 4 miles per hour when loaded, and 8 miles per hour when empty. They are generally rated to carry a normal load of approximately 2 tons, and will negotiate gradients of one in ten. A storage battery truck will replace from four to six men on a haul of 200 to 800 feet. The running cost, including maintenance, interest, and depreciation, is approximately 16s. per working day of eight hours.

"The Eclipse" Automatic Loading Shovel.—This device is a very suitable means for bringing the rock phosphate from the store to the grinding plant. It consists of a Fordson Tractor with a loading shovel attached. The shovel will pick up a load of 10 cwt, and as will be seen in the illustration Fig. 117 there is no turning; the machine travels straight from the heap to the crusher. The shovel does not obstruct the driver's view. The thrust, due to filling, is taken directly by the back axle through the main frame below the centre of gravity; and the shovel is not lifted directly, but is pulled up an incline on rollers.

Hand-propelled monorails are sometimes used for bringing the phosphate rock from the store to the grinding plant.

For the storing of phosphate rock and superphosphate, it is absolutely necessary to transport at a considerable height from the ground, and when a monorail system is used for this purpose, the skips are operated either by mechanical or electrical haulage, and automatic tipping devices are arranged at suitable points for emptying the skips.

Electric Telfer.—The telfer system was invented by the late Professor Fleming Jenkin in 1882. The name was chosen by himself from the Greek—tele—far, and pherein—to carry. Fleming Jenkin is better known to-day as the intimate friend of R. L. Stevenson the novelist, than as the inventor of the telfer.

A telfer consists of a trolley running on a single rail and propelled by an electric motor which collects its current from overhead wires supported alongside the track. A receptacle is suspended from the trolley for carrying the load. There is no limit to the distance which the load may be carried, and the telfer may be arranged to work automatically—that is, after picking up its load, it travels to a predetermined position, tips its load, and returns empty to the starting-point; or it may be equipped with a cab, which accommodates an operator who controls all the movements of travelling, tipping, and raising or lowering the skip, as shown in Fig. 119.

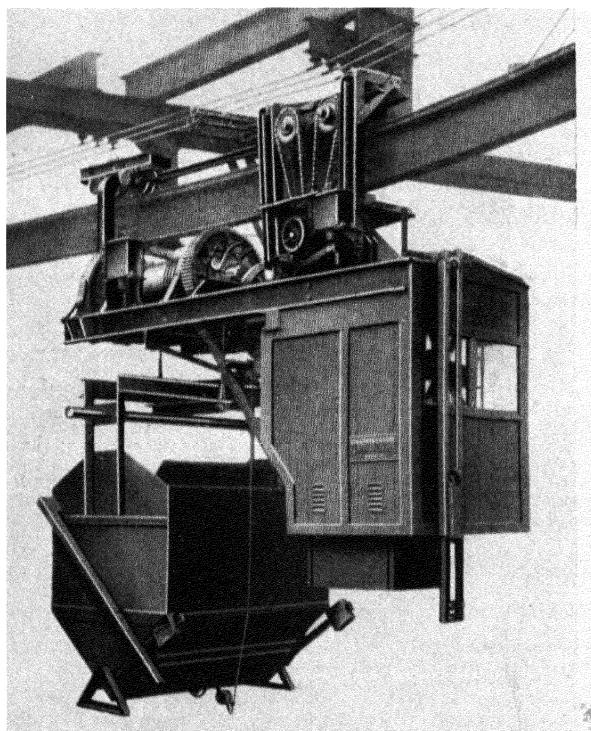


FIG. 119.—MAN-OPERATED TELPHER

The telfer cars are loaded from two existing bucket elevators, one of which conveys the compound fertiliser, whereas the other handles the superphosphate.

The discharge takes place along six parallel tracks and in order to make the routes over which the cars travel as short as possible, five loop lines with an appropriate number of switch points have been provided for. Each of the telfer cars is equipped with its own travelling motor of about $\frac{1}{2}$ h.p., suitable for a travelling speed of about 235 feet per minute, and the bottom discharge buckets have a capacity of $17\frac{1}{2}$ cubic feet each, containing about 1,000 to 1,250 lb. of material.

With the object of maintaining the necessary spacing between the cars along the track, thus obviating the likelihood of a collision, an automatic blocking system is employed. For this purpose conductive wiring of the plant is interrupted and is divided into a number of sections, the length of which is determined by the hourly capacity for which the plant has been designed. At the end of

Telfers are usually designed to travel either on the top or bottom flange of a rolled steel joist, and can negotiate curves of very small radius from 15 to 18 feet.

When fitted with a grab bucket, a telfer system is very suitable for unloading barges or railway trucks. Loads up to 3 tons may be carried at a speed of 6 to 10 miles per hour: the hoisting speed is from 60 to 100 feet per minute.

There is a very interesting automatic telfer plant which has recently been installed at the works of the West Norfolk Farmers' Manure & Chemical Co-operative Co., Ltd., King's Lynn, and supplied by Bleichert Mitchell, Ltd.

The layout of the plant is shown in Fig. 120.

The duty of the plant is the transport of superphosphate and compound fertiliser and its distribution over a number of sheds.

each section of conductor wires a blocking switch is fitted which is actuated by the passing car. With the aid of these switches the telfer car switches off the current from the section which it has just left and switches it on again only after it has passed over the next following blocking section. Irrespective of whether the car is travelling or at a standstill there is invariably a dead section behind every car over which the next car cannot approach the one in front.

The various rail points which are incorporated into the track and which occasionally have to be set by hand, according to the shed at which the discharge is to take place at any given period, are also fitted with blocking switches so as to make derailment of the cars impossible should the points be inadvertently set wrongly. Immediately a rail point is set by hand the electric current is switched off on the open section and any telfer car which might be approaching this section will immediately come to a standstill. It can only resume its travel after the point is placed in its proper position by the man on duty, thereby again closing the circuit.

A further problem arose owing to the fact that two levels had to be traversed, the loading valves being at a high level, and the various sheds being on the low level. Since a new bridge had to be erected, connecting the various buildings and accommodating the telfer plant, it was decided to build part of the bridge at an incline. A haulage chain has been installed, which is driven by its own motor, and which hauls the empty cars up to the high level and releases the loaded cars to the low level. The chain engages into forks with which each telfer car is equipped.

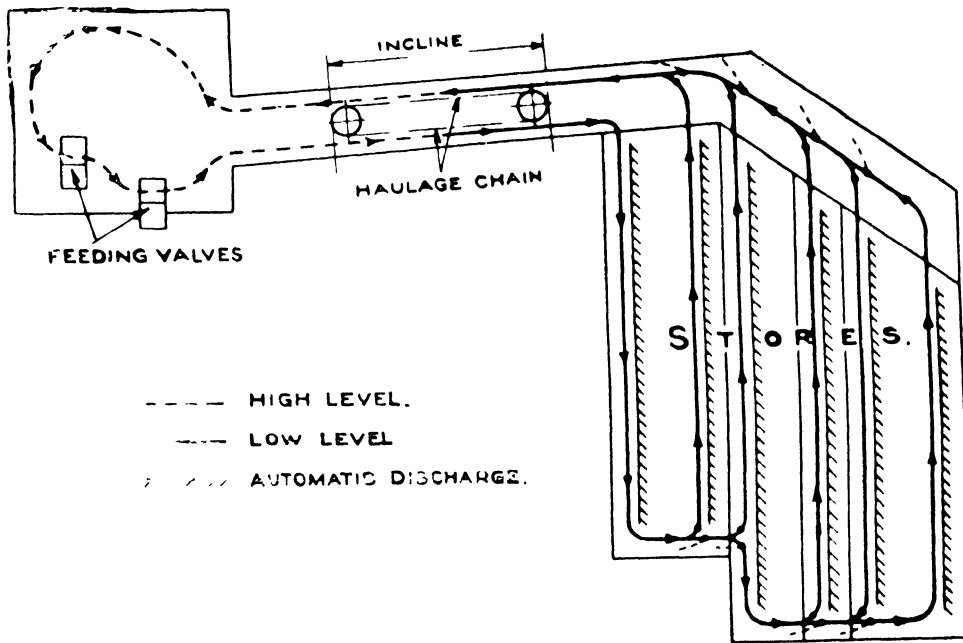


Fig. 120.—LAYOUT OF BLEICHERT TELPHER PLANT

order to prevent any undue fluctuations of the travelling speed whilst operating over the chain haulage section, the blocking system is arranged in such a way that a returning empty car awaits the arrival of the loaded car before entering this chain section.

The discharge of the telfer buckets is fully automatic. The release lever, which is fitted to each telfer car, strikes against a detent, thus releasing the locking device operating the flap bottom. The detent is fitted to a travelling gear, which can be placed in any desired position by means of a rope winch, the whole arrangement being shown in illustration Fig. 122. Each discharge section is equipped with one of these travelling trip gears.

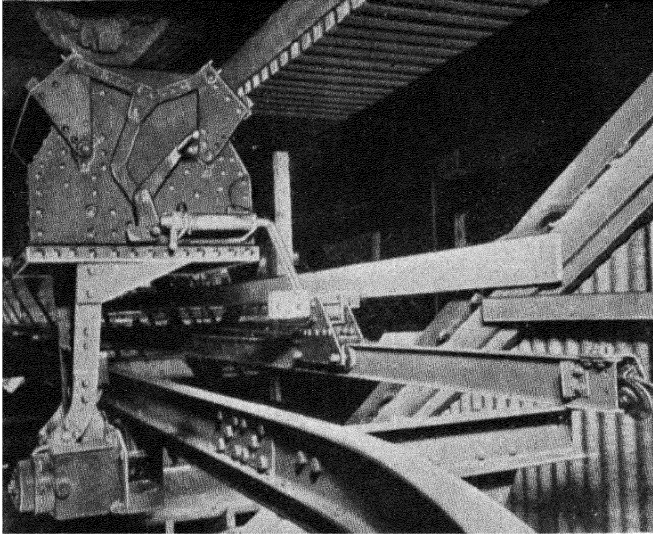


FIG. 121. - TELPHER BUCKET DISCHARGING

travelling detent does not require any regular attendance as its position needs to be altered at long intervals only, according to the progress of dumping in the sheds. The same holds good for the setting of the rail points, since they can remain in their position until a shed is completely filled or until the other material has to be dealt with.

The total length of track is about 2,000 feet, and the plant has been designed for an initial capacity of 20 tons per hour. The blocking system, however, has been arranged for a final capacity of 30 tons per hour.

Overhead Crane.—The overhead travelling crane with grab has been referred to and illustrated in previous chapters.

This method of transportation requires a specially designed building, and is only applicable where the production approximates to 80,000 tons per annum or over. Where these cranes are installed, the span of the storage building is usually from 60 to 75 feet. The largest grab bucket has a capacity of 94 cubic feet, and will pick up in one lift 5 tons of rock or 3 tons of superphosphate.

These cranes are capable of moving large quantities of material in a short time, approximating from 50 to 100 tons per hour, depending upon the distances they have to travel with their loads.

In some of the large American works, overhead travelling cranes are practically the only means employed for the mechanical handling of the materials. They store the phosphate rock, bring it to the grinding plant, excavate the dens, store the superphosphate, and bring all materials to the superphosphate dressing and shipping units.

The telpher cars returning empty from the sheds are automatically brought to a standstill just before approaching the loading valves of the feeding bucket elevators. On illustration Fig. 122 two pull handles can be seen, and the telpher cars can only enter the suspension rail underneath the loading hopper after one of these has been manipulated by the operator. The despatch of the loaded telpher cars is effected in a similar manner by operating the second pull switch, this being the only manual labour required.

To operate the plant, therefore, an exceedingly small staff is needed, since the only manual labour necessary is for the loading of the telpher buckets from the feeding valves of the bucket elevators. The manipulation of the

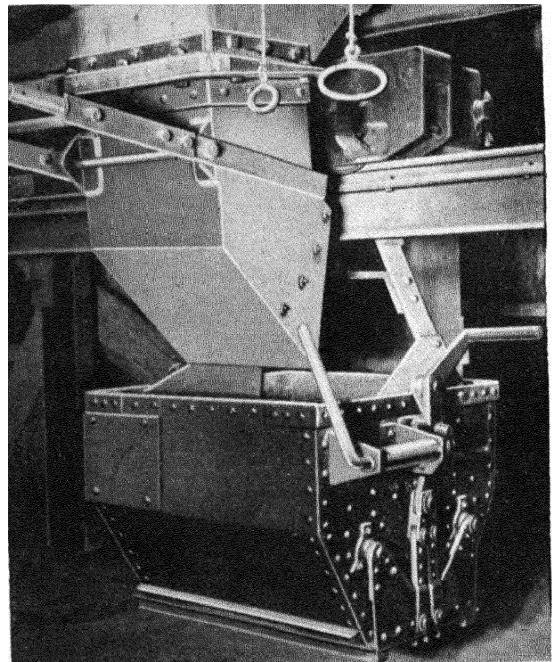


FIG. 122.—TELPHER BUCKET LOADING

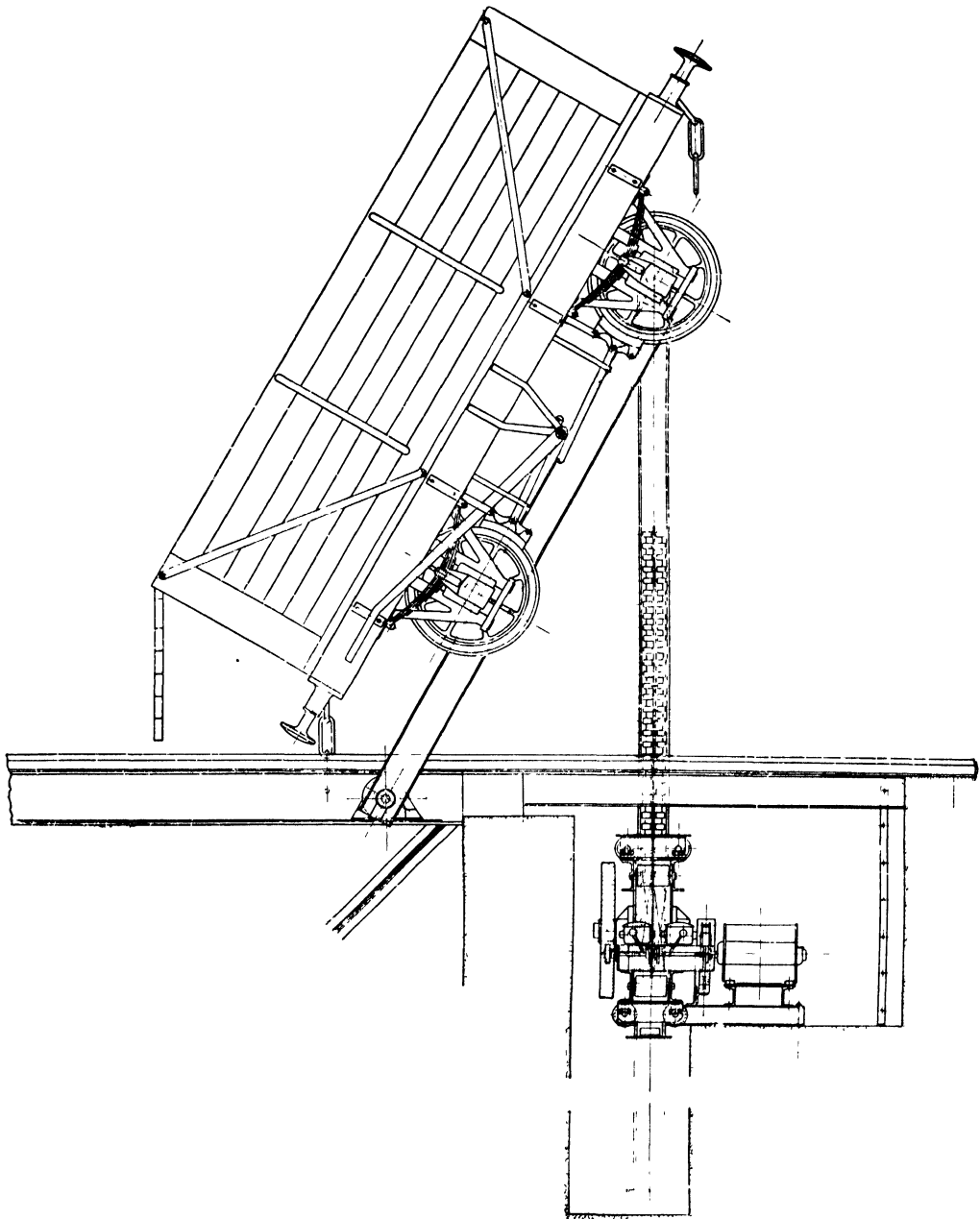


FIG. 123.—BABCOCK & WILCOX TIPPING RAM FOR WAGONS

In some plants where overhead cranes are employed, the cost of labour for discharging and piling phosphate rock is approximately 3d. per ton, and for batching and dressing superphosphate, approximately 6d. per ton. These are 1939 figures.

In British works, portable jib-cranes with grabs are being used in several instances for unloading barges and railway wagons. This is an economical method if the quantities of materials to be handled justify the initial outlay. Such cranes handle from 50 to 70 tons per hour.

Conveyors used for transporting materials in small units or in a continuous stream are many and varied. In a fertiliser works the types commonly used are : chain and bucket elevators, rubber belt conveyors, steel belt conveyors, gravity bucket conveyors, and worm conveyors. The first four are used for handling the rock phosphate and other raw materials. Steel tray conveyors are most suitable for conveying the superphosphate, and worm conveyors are extensively used for conveying the ground phosphate.

In works where the rock phosphate is delivered by rail, considerable labour is often employed in emptying the wagons by hand. This hand-shovelling process often determines the capacity of the conveying plant, although it may have been designed to handle twice as much material per hour as it actually receives. Only two men at one time can conveniently shovel material out of a 10-ton wagon, fitted with dropping side doors, and it usually takes half an hour to discharge a wagon in this way, which is slow and costly.

Electric tipping rams, are now employed for this work, which effect a saving in time and labour. They necessitate the use of wagons with hinged ends. The wagon is tipped up on end by means of a cradle which engages with one of the axles. The cradle is raised and lowered mechanically, through gearing driven by an electric motor.

A device of this kind, made by Babcock & Wilcox, is shown in Fig. 123.

The ram is placed in line with the receiving hopper of the conveying plant, so that as the material falls out of the wagon it is received into the conveying system, and withdrawn from the hopper at the rate of the plant's maximum capacity.

The cradle is so designed that the front wheels of the wagon are lifted clear of the running rails to permit of the wagon being hoisted to an angle of 55° without the buffers fouling the rails.

Chain and bucket elevators are extensively used for handling rock phosphate in all countries. They are employed for storing the phosphate, and most grinding systems include a circulating elevator.

Unless properly designed for the duty required, elevators can be a great source of trouble, and the cause of serious stoppages of the whole plant. When an elevator breaks down it is usually the fault of the chain. A sufficient margin of strength may not have been allowed in the first instance, and, owing to the rapid wear of overstrained parts, the chain suddenly breaks and, without warning, there is a heap of twisted buckets and chain at the bottom of the elevator casing.

This is not very likely to occur if two strands of chain are used, and for elevators exceeding 50 feet in centres, and rated at a normal capacity of 50 tons per hour or over, two chains are essential.

There are many types of chain to select from, including plain cable chains, stamped link chains, and pin chains made of malleable iron or steel.

In all cases with cable chains, the buckets are secured to two strands with C type attachments. Cable chains are particularly suitable for superphosphate elevators, and are extensively used for this purpose.

Buckets of various types are used. The stamped, seamless bucket is both light and strong, and, when fitted with a reinforced lip, is very durable. Malleable iron buckets will stand more wear, but are much heavier. Continuous buckets are now extensively employed ; they increase the capacity of the elevator without enlarging the casing, and they prevent the material which is

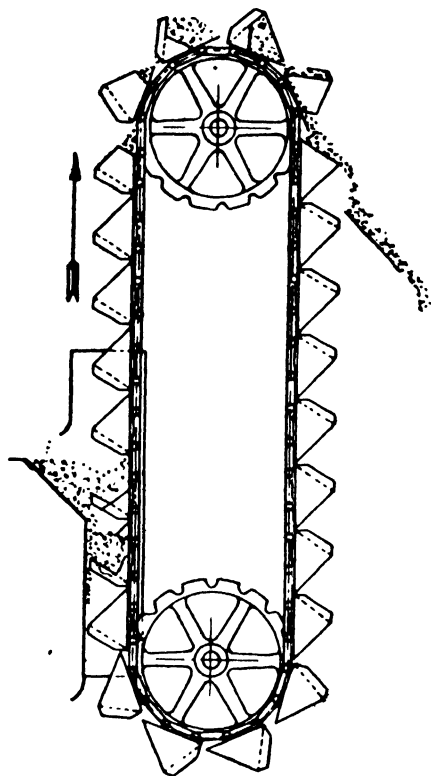


Fig. 124.—CONTINUOUS BUCKET ELEVATOR

being elevated from getting around the chainlinks and causing undue wear. There is practically no dredging action in a properly designed continuous bucket elevator, which further minimises the wear on the buckets.

A continuous bucket elevator discharges better at the top, and there is little tendency for the material to be thrown down the back. This is clearly shown in Fig. 124.

The table on page 202 gives the normal capacities of elevators handling rock phosphate.

Continuous bucket elevators, with buckets of similar width, have capacities approximately 75 per cent greater than the above.

Fig. 125 shows an elevator of the perfect discharge type. The buckets are secured to double-strand chains attached to the sides of the buckets. The chains are usually of the crane type, with C attachment links, and as shown in the illustration, the buckets bend back under the top sprocket which ensures that all material is delivered to the chute without spilling down the back of the elevator.

If possible, in fertiliser works, all elevators should be made vertical so as to dispense with skidder bars, which increase the friction with consequent wear and tear.

Belt conveyors are particularly suitable for conveying materials long distances.

They are used in many fertiliser works for storing the rock phosphate when the railway-siding is some distance from the store.

They require very little power, and the maintenance costs are low. The speed at which the belt runs is approximately 250 feet per minute. Troughed belts are generally employed, as they convey more than a flat belt of the same width without spilling. When troughed, a belt of stepped-ply construction is used, which has a greater number of plies at the edges of the belt than at the centre, and the rubber cover is thicker at the centre than at the edges, in order to withstand the greater abrasion.

A belt made thus is flexible across its width, allowing it to conform to the shape of the trough formed by the idlers. It is stiff longitudinally, as the extra number of plies at the edges act as a truss and prevent sagging between the idlers. The design of the troughing rollers is very important, as the belt should be allowed to trough in a natural manner, which minimises wear.

The Robins patent troughing idlers are so designed that the profile of the belt nearly approaches the arc of a circle. This type of idler is shown in Fig. 126 and consists of a series of cast-iron pulleys turning on hollow shafts made of cold, drawn, seamless steel tubing. Large compression grease caps are fitted on the end shafts, and force the grease through the continuous lubricating passage and out through holes drilled in the tubes.

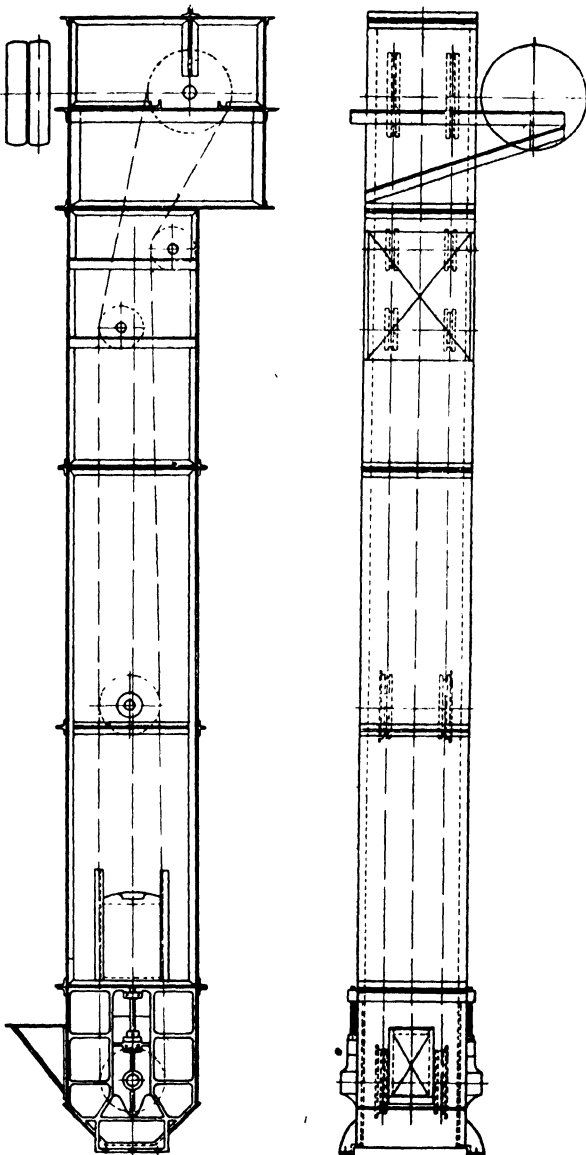


FIG 125.—“PERFECT DISCHARGE” ELEVATOR

TABLE 49

Vertical Elevators

Width of bucket. Ins.	Cubic capacity of buckets. Cub. ins.	Pitch of buckets. Ins.	Speed of elevator chain. Ft. per min.	Type of chain.	Capacity tons per hour rock phosphate.	Working stress of chain in lb.
8	160	15	160	603 bushed	15	2,500
10	200	16	160	604 "	20	3,500
12	320	16	160	604 "	30	3,500
14	400	18	150	600 "	35	4,000
15	450	18	150	600 "	40	4,000
18	750	18	140	Two strands 600 bushed	65	8,000
20	900	18	140	"	80	8,000
24	1,300	18	140	"	115	8,000

These idler pulleys may be mounted on roller bearings, which diminish the power and reduce the stress on the belt, so that a belt with a smaller number of plies may be used.

When conveying phosphate rock, belt conveyors will operate quite satisfactorily at an angle of 18° to 20°. If the phosphate contains a large percentage of fine material, the angle may be increased to 22°, but the angle is governed largely by the manner of feeding the belt, as a uniformly loaded conveyor can be inclined at a greater angle than one on which the load is intermittent.

The following table gives the capacities of troughed belt conveyors handling phosphate rock :

TABLE 50

Width of belt. Ins.	Maximum size of material. Ins.	Speed. Ft. per min.	Capacity. Tons per hour.
12	2	250	30
14	2½	250	40
16	3	250	50
18	4	250	65
20	5	250	80
22	6	250	90
24	8	250	110
30	10	250	180
36	12	250	260

When a belt conveyor is used for filling the phosphate store, an automatic tripper is employed for distributing the phosphate along the entire length of the building.

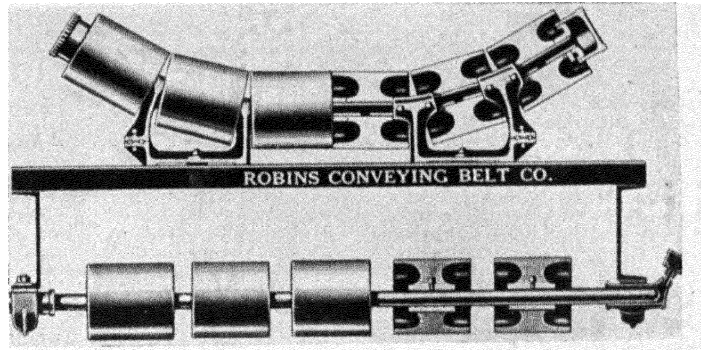


FIG. 126.—ROBINS TROUGHING IDLERS

Fig. 127 shows a Robins automatic tripper, which is used for discharging the phosphate from the belt at any desired point. The tripper is propelled by the conveyor belt itself, power being transmitted to the axles of the carriage through bevel and worm gearing. The tripper travels forwards and backwards between any two points, and reverses its direction automatically at the end of each run. By throwing the travelling mechanism out of gear, the tripper will operate from a stationary position. The discharge chute is generally arranged to throw off the material on both sides of the conveyor.

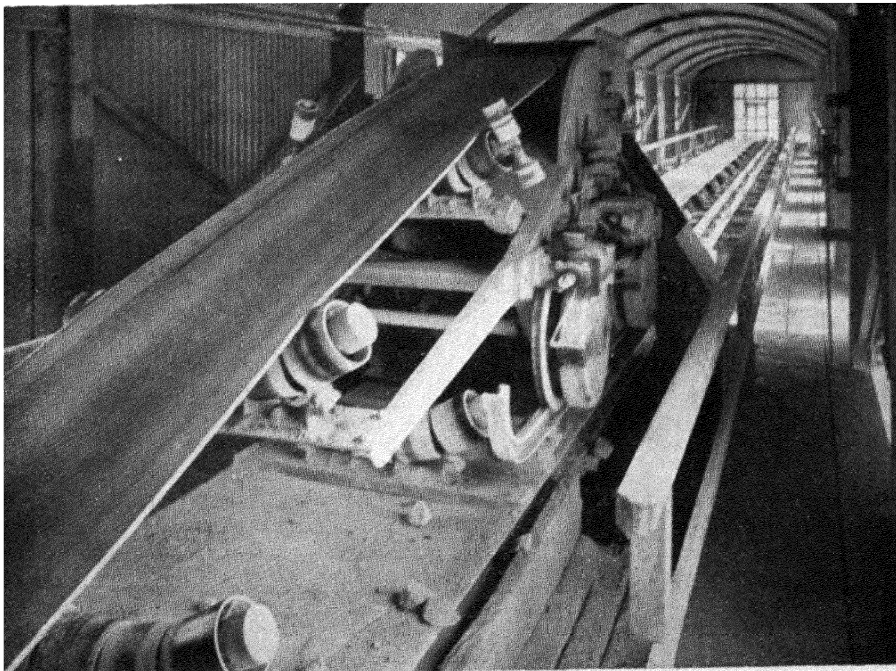


FIG. 127.—ROBINS AUTOMATIC TRIPPER

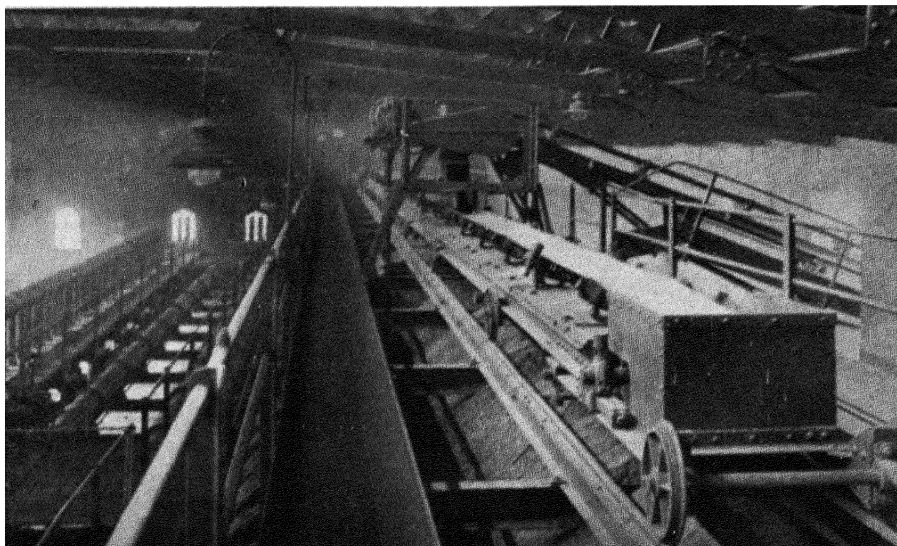


FIG. 128.—ROBINS SHUTTLE BELT CONVEYOR

If the phosphate store is placed in such a position in relation to the railway-siding that the rock is delivered either by elevator or conveyor at a central point in the length of the storage building, the distribution along the entire length of the store is then effected by means of a shuttle belt conveyor (see Fig. 128).

A conveyor of this type is mounted on a chassis, and its length is a little more than half the length of the store building. The belt travels in both directions, and so does the chassis carrying the conveyor. The complete conveyor travels to and fro on a track like a shuttle, and automatically reverses at the end of its travel. The belt runs in the opposite direction to the chassis, so that the phosphate is always being delivered over the rear of the carriage, and as the carriage reverses, the belt reverses also.

This type of distributor can also be used in a stationary position if required.

Steel belt conveyors are a comparatively recent introduction, and employ a flexible steel band in place of the textile and rubber belt previously referred to. These belts when made of rustless steel have proved to be very resistant to corrosion.

The speed at which the belt runs is approximately 200 to 250 feet per minute. The belt is joined either by a lap-riveted or, where a flush surface is preferable, a butt-strapped joint. These belts vary in thickness from 0.4 to 1.1 mm.

One special feature of this type of belt is the simple unloading facilities. No throw-off carriage is required for intermediate discharging, as this is effected by scraper ploughs.

The general principle of a scraper plough is a number of steel blades, each about 6 inches long by $3\frac{1}{4}$ inches wide by 0.04 inch thick, secured to a bar, each blade overlapping the next about $\frac{3}{4}$ inch, so giving a laminated effect and pressing edge downwards on the belt. These are arranged obliquely across the belt, discharging to one side or the other, or V-shaped if unloading on both sides simultaneously.

These belts are used to convey superphosphate, and, as the nature of the belt enables it to withstand close scraping, there is no tendency for the material to cling and paste, and corrosion is reduced to a minimum. They are not affected by the temperature of the superphosphate if it is hot, as they are not unduly affected by temperature up to 250° F.

A belt 16 inches wide will convey approximately 30 tons of superphosphate per hour.

Gravity bucket conveyors are not extensively used in British fertiliser works, as the annual production of the average-sized works does not justify the initial outlay.

For capacities ranging from 50 to 100 tons per hour this type of conveyor has many advantages. It transports the material vertically, horizontally, or on an incline without spilling.

In most unloading plants for phosphate rock the material has to change its direction several times, which necessitates several different elevators or conveyors. This change of direction is effected in the gravity bucket conveyor without increasing the mechanical units.

It operates slowly and quietly, and requires very little attention. The unloading is done anywhere on the lower horizontal run, through a feeding device, to ensure uniform loading.

The material is discharged anywhere to suit conditions, by means of stationary or movable trippers. When these tripper arms are raised to the operating position, the cams on the side of the buckets come in contact with them, and each bucket is made to tip through an angle of about 120° , so that the contents are efficiently discharged (see Fig. 129).

When the direction of the conveyor is changed from the horizontal to the vertical, or vice versa, frictional resistance is overcome by the use of revolving wheel curves of large diameter.

The chain consists of two double-link bushed chains: each link is made of flat steel, and they form pairs by means of stud rivet distance pieces: the bushes are case hardened. There is an automatic lubricating device for oiling the chain while the conveyor is working.

The loading is effected by means of a special rotary filler. It consists of a hollow casting with five openings in its periphery, arranged to centre with the buckets when

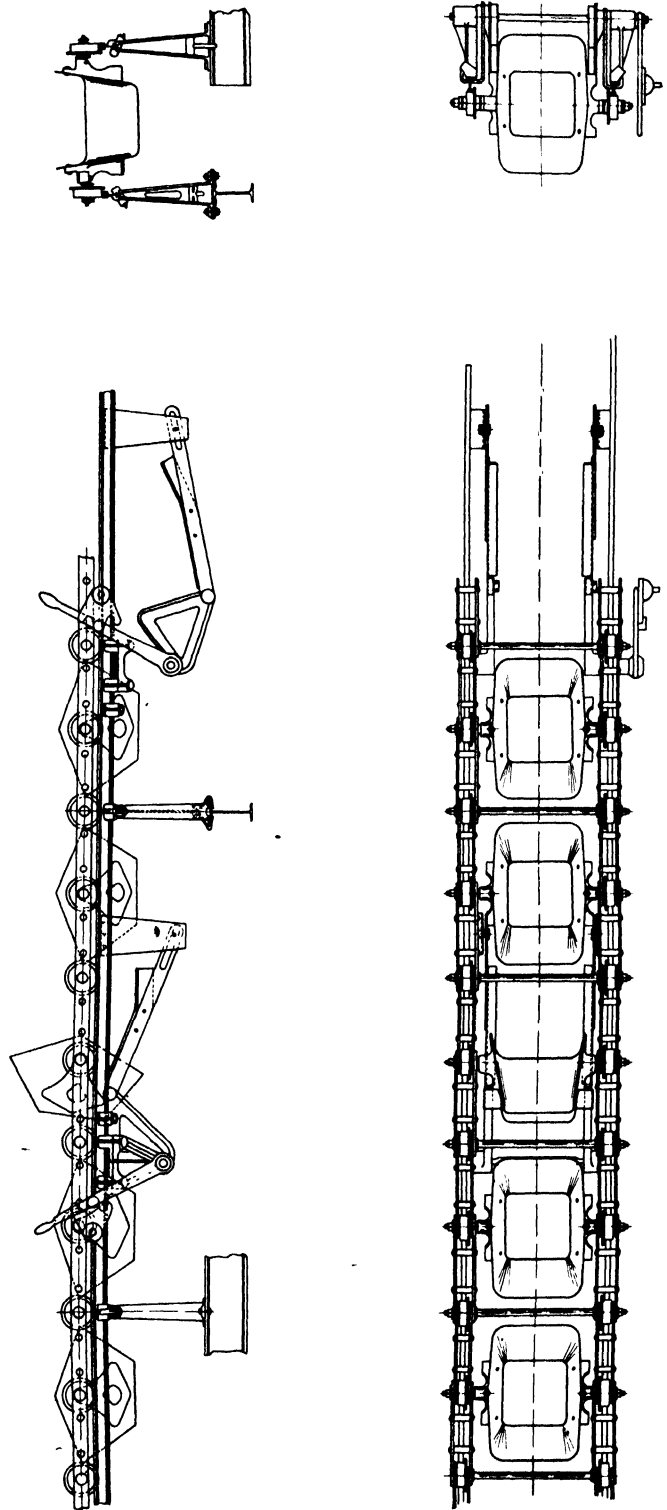


Fig. 129.—GRAVITY BUCKET CONVEYOR

rotating; the material is fed into the centre of the filler and passes out through the peripheral openings into the conveyor buckets.

Redler's Conveyors are now extensively used in fertiliser works and there are several types. The Redler system is unique, in that it is a distinct departure from all previous types of conveyors.

It consists of a trough and chain working therein, and capable of carrying a load of a depth approximately the equivalent of the width of the chain, the load travelling at the same speed as the chain. Not only is this effected horizontally, but by providing specially designed chains, the conveying can be inclined or vertical.

The illustration, Fig. 130, which is a photograph of a model made in celluloid, makes clear what is hard to believe until one sees it in practice.

Redler conveyors are slow-running. The average speed is approximately 60 feet per minute, hence they are suitable for conveying ground phosphate, as they are practically dustless in operation. They absorb comparatively little power. They occupy less space than chain and bucket elevators, and it is not possible to overload them.

The illustration, Fig. 131, shows a Redler conveyor combining a horizontal and inclined run. The motor for driving same is mounted on top of the trough near the delivery end. The trough, being in the form of a box girder, dispenses with intermediate supports except in the case of long conveyors.

Worm Conveyors are extensively used for conveying the ground phosphate, and are particularly suitable for this class of work: they make very little dust when working, as they convey the material without much agitation. When enclosed in dust-tight steel or cast-iron casings they are practically dustless.

The type of worm conveyor commonly used is known as the Archimedian screw conveyor. The blades, which are made of steel plate, are pressed into the shape of a helix and fit closely round the shaft. Occasionally the blades are made of cast iron in short sections, and are then mounted on a square shaft. In steel blade conveyors the shaft is generally made of steel tube, with solid steel gudgeons fitted at intervals where the bearings are situated. It

is important that the bearings are not placed too far apart, otherwise the screw is liable to get out of truth.

The spiral conveyor has the disadvantage that the intermediate bearings are partially covered by the ground phosphate which is being conveyed. This is obviated to a large extent by the use of a bearing of the dust-proof type.

Worm bearings should be lubricated with stauffer grease, as it provides a film round the outer edges of the journal, which tends to make a seal against the entrance of dust.

Worm conveyors will convey on an incline, and many are working on ground phosphate at an incline of 20°.

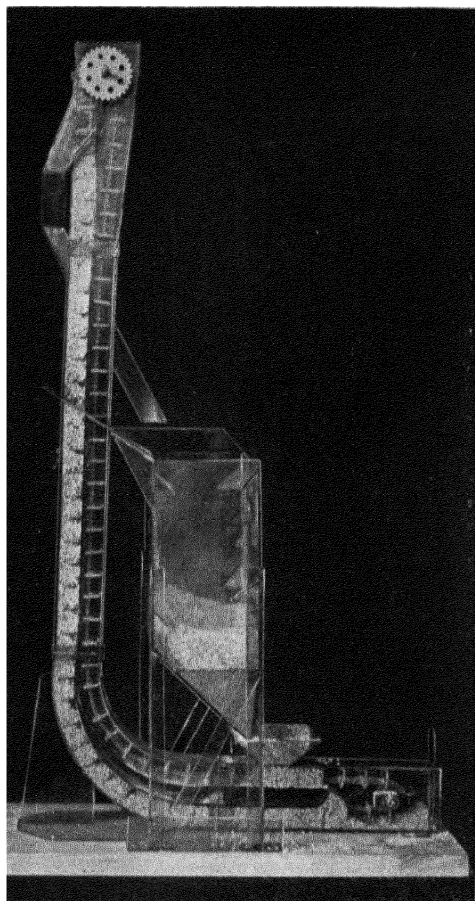


FIG. 130.- MODEL OF REDLER CONVEYOR

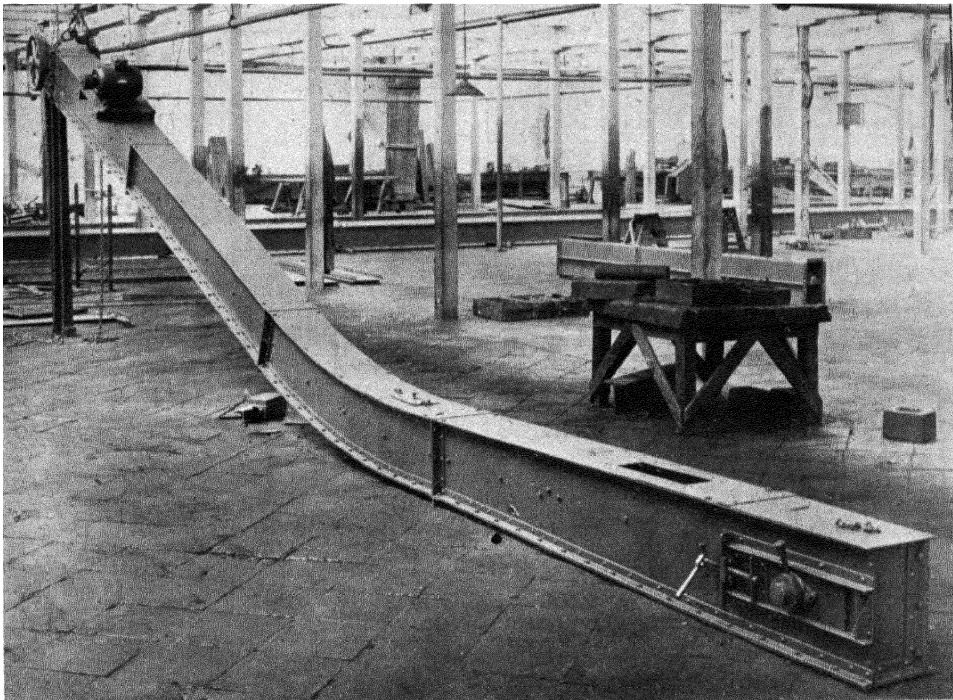


FIG. 131.—REDLER CONVEYOR

The following table gives the capacities of Redler conveyors.

TABLE 51

Chain speed 60ft. per min. max.	DENSITIES OF MATERIALS PER CUBIC FOOT IN LB.													
	100	90	80	70	60	50	45	40	35	30	25	20	15	10
Size of con- veyor.	CAPACITY IN TONS PER HOUR.													
3"	8	7 $\frac{1}{4}$	6 $\frac{1}{2}$	5 $\frac{1}{2}$	4 $\frac{3}{4}$	4	3 $\frac{1}{2}$	3 $\frac{1}{4}$	2 $\frac{3}{4}$	2 $\frac{1}{2}$	2	1 $\frac{1}{2}$	1 $\frac{1}{4}$	3 $\frac{3}{4}$
4"	14 $\frac{1}{2}$	12 $\frac{3}{4}$	11 $\frac{1}{2}$	10	8 $\frac{1}{2}$	7 $\frac{1}{4}$	6 $\frac{1}{2}$	5 $\frac{3}{4}$	5	4 $\frac{1}{2}$	3 $\frac{1}{2}$	2 $\frac{3}{4}$	2 $\frac{1}{4}$	1 $\frac{1}{2}$
5"	22	19 $\frac{3}{4}$	17 $\frac{1}{2}$	15 $\frac{1}{2}$	13 $\frac{1}{4}$	11 $\frac{1}{4}$	10	8 $\frac{3}{4}$	7 $\frac{1}{2}$	6 $\frac{1}{2}$	5 $\frac{1}{2}$	4 $\frac{1}{2}$	3 $\frac{1}{4}$	2 $\frac{1}{4}$
6"	32	28 $\frac{3}{4}$	25 $\frac{1}{2}$	22 $\frac{1}{2}$	19 $\frac{1}{4}$	16	14 $\frac{1}{2}$	12 $\frac{3}{4}$	11 $\frac{1}{4}$	9 $\frac{1}{2}$	8	6 $\frac{1}{2}$	4 $\frac{3}{4}$	3 $\frac{1}{4}$
7"	44	39 $\frac{1}{2}$	35 $\frac{1}{4}$	30 $\frac{3}{4}$	26 $\frac{1}{2}$	22	19 $\frac{1}{2}$	17 $\frac{1}{4}$	15 $\frac{1}{2}$	13 $\frac{1}{2}$	10 $\frac{3}{4}$	8 $\frac{3}{4}$	6 $\frac{1}{2}$	4 $\frac{1}{2}$
8"	57 $\frac{1}{2}$	50	45 $\frac{3}{4}$	40	34 $\frac{1}{2}$	28 $\frac{1}{2}$	25 $\frac{3}{4}$	22 $\frac{3}{4}$	20	17 $\frac{1}{4}$	14 $\frac{1}{2}$	11 $\frac{1}{2}$	8 $\frac{1}{2}$	5 $\frac{3}{4}$
9"	72	65	57 $\frac{1}{2}$	50 $\frac{1}{2}$	43 $\frac{1}{2}$	36	32 $\frac{1}{2}$	28 $\frac{3}{4}$	25 $\frac{1}{4}$	21 $\frac{1}{2}$	18	14 $\frac{1}{2}$	10 $\frac{3}{4}$	7 $\frac{1}{4}$
11"	108	97	86 $\frac{1}{2}$	76	64 $\frac{1}{2}$	53 $\frac{1}{2}$	48 $\frac{3}{4}$	43 $\frac{1}{4}$	37 $\frac{1}{2}$	32 $\frac{1}{2}$	25 $\frac{3}{4}$	21 $\frac{1}{2}$	16	10 $\frac{3}{4}$
13"	150	135	120	105	89 $\frac{1}{2}$	75 $\frac{1}{4}$	67 $\frac{1}{4}$	60	52 $\frac{3}{4}$	44 $\frac{3}{4}$	37 $\frac{1}{2}$	30	22 $\frac{1}{2}$	14 $\frac{3}{4}$
15"	198	180	160	140	120	100	89 $\frac{1}{2}$	80	69 $\frac{1}{2}$	60	49 $\frac{1}{2}$	40	29 $\frac{1}{2}$	19 $\frac{1}{2}$
17"	256	230	205	180	155	128	115	102	89 $\frac{1}{2}$	76 $\frac{3}{4}$	64	51 $\frac{1}{4}$	38 $\frac{1}{2}$	25 $\frac{1}{2}$

The following table gives normal capacities, etc., of Archimedian screw conveyors :

TABLE 52

Diameter of spiral. Inches.	Pitch of screw. Inches.	Revolutions per min.	Tons of ground phosphate conveyed per hour.
6	4	90	4
8	6	80	7
10	7	70	12
12	8	60	15
14	9	60	18
15	10	60	20
18	11	50	25

The horse-power may be arrived at by using the formula :

$$H.p = \frac{W \times L \times C}{33,000}$$

W=weight in lb. of phosphate moved per minute.

L=length of conveyor in feet.

C=constant for ground phosphate=2.75.

Steel Tray Conveyors are chiefly used in fertiliser works for handling the superphosphate.

In Chapter VI, dealing with mechanical dens and excavators, reference has been made to this type of conveyor for removing the superphosphate as it is cut from the den.

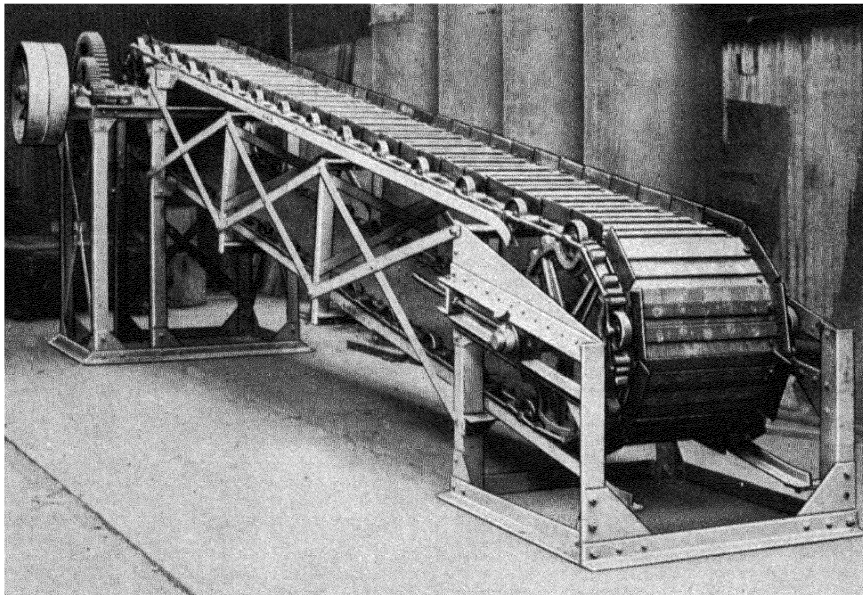


FIG. 132 —STEEL TRAY CONVEYOR

Being made of steel, they are not affected by the temperature of the hot material, and they may be used to convey horizontally or on an incline, according to local conditions.

Fig. 132 shows a steel tray conveyor working in conjunction with a Wenk den.

The trays are generally about 18 inches wide, with sides bent up about 4 inches.

They overlap one another about 1 inch, and are mounted on two strands of chain, which are underneath the trays. Every second tray has a pair of rollers, one at each side, which run on rail tracks, and these rollers keep the surface of the trays level and prevent spilling between the joints.

When the inclination of the conveyor is more than 30° , the trays are fitted with backs to prevent the superphosphate from sliding back. Owing to the pasty nature of the material being conveyed, the trays become coated with the superphosphate, and all of it is not discharged at the delivery end. The superphosphate which still adheres has a tendency to fall off the trays as they travel along the bottom run of the conveyor. This spilling is a nuisance, and sometimes amounts to quite a lot of material which has to be collected.

To obviate this trouble, a tapping device is often arranged at the delivery end, and as each tray passes a certain point, it receives a blow on the back, which helps to dislodge the superphosphate which is tending to adhere.

For the same purpose a scraper is also used, arranged on a balance weight; but this latter device cannot be used when the trays are fitted with backs.

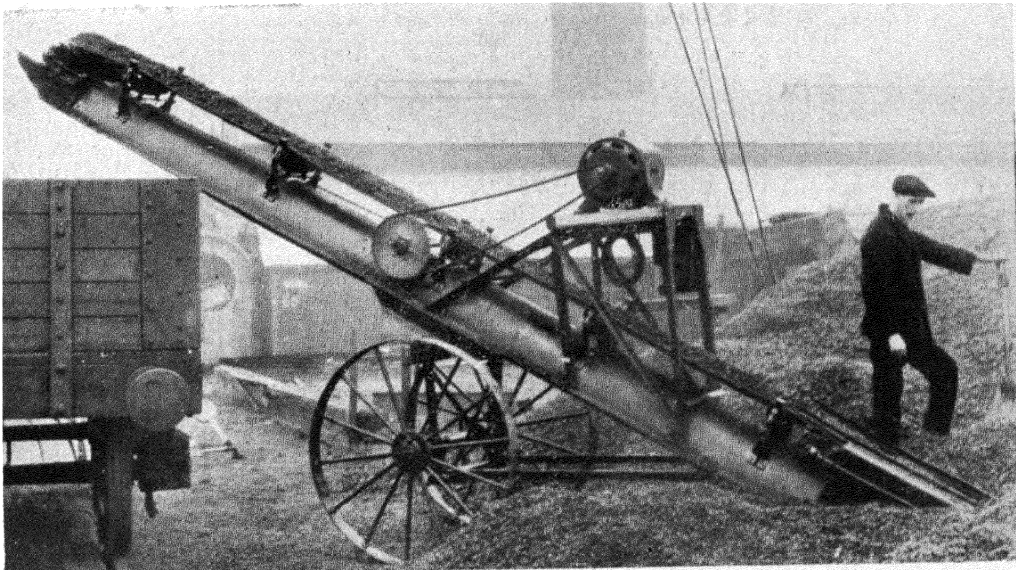


FIG. 133.—PORTABLE BELT CONVEYOR

Portable Conveyors, as illustrated in Fig. 133, are used for handling fertiliser materials in bulk or in sacks.

The complete conveyor is mounted on a wheeled truck, which renders it easily portable, and in some cases there is a jib structure for raising or lowering the delivery end of the conveyor. These conveyors may operate with a canvas and rubber belt or with steel trays.

For most fertiliser materials, the maximum angle of inclination when conveying in bulk is approximately 25° . A steel tray conveyor when fitted with trays with short backs will handle bulk material at an angle of 45° , but at a reduced capacity.

Under average conditions of loading, the following capacities dealing with bulk material can be obtained :

Width of belt.	Capacity in tons per hour.	
	Phosphate rock.	Sulphate of ammonia.
18 inches	50	45
24 ,,	80	75

Portable conveyors are very suitable for unloading phosphate from wagons, if the store is not too far distant from the unloading point- say 50 feet.

In many works, unloading is effected by shovelling from the truck into barrows, and then wheeling the barrows up an inclined runway and dumping on the pile. A portable conveyor will save the labour of five men when employed on work of this nature.

Portable conveyors are extensively used for sack piling and also for loading sacks into trucks. There is no possibility of the sacks being damaged, and it is possible to load or pile 500 sacks per hour.

Fig. 134 shows a portable conveyor for sack stacking. It is reversible and can also be used for lowering the sacks again to the ground level.

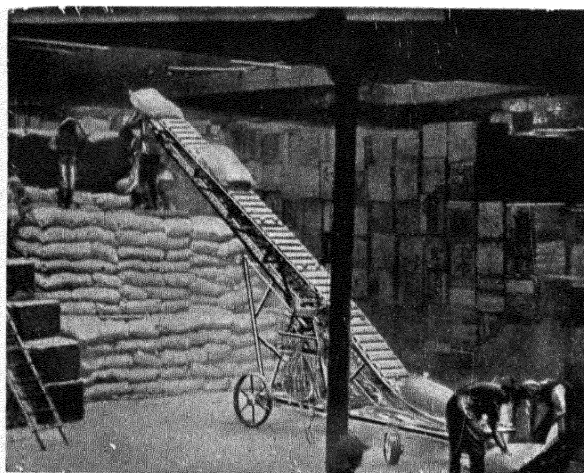


FIG. 134. —SACK-STACKING CONVEYOR

CHAPTER XVII

CRYSTALLISATION AND GRANULATION OF FERTILISER PRODUCTS

WITH the advent of the Haber synthetic ammonia process in Germany, and the developments incidental to the production of sulphate of ammonia by that process, it became evident that the sulphate of ammonia of the future would need to be improved. The obvious requirements would be a crystalline product, neutral, practically free from moisture and of better colour than that hitherto produced at the gasworks and coke-ovens in the various countries of the world.

It must be recalled that the Badische Anilin und Sodafabrik were starting with pure chemical reagents, such as gaseous nitrogen and hydrogen and sulphuric acid manufactured by the contact process, and hence their final product was of first quality. Various processes were introduced during the period 1915 to 1918 for the production of a neutral salt with specific physical properties, and it is only necessary to recall the names of Adams, Capron, Lessing, Linder and Sheard to reveal the many processes which were devised for meeting the end in view.

But **with** the adoption of neutralising and drying processes for the manufacture of sulphate of ammonia, representing the first stage in the production of a better quality of sulphate of ammonia, there gradually developed a demand for a larger-sized crystal. Many processes have been developed, and many patents granted, for producing sulphate of ammonia of large grain size. One of the authors (Parrish) has had a wide experience of the manufacture of sulphate of ammonia of large crystal size, and is convinced that with the usual qualities of sulphuric acid available in Great Britain and European countries there should be no difficulty in the production of such large-sized crystals, provided the saturators are satisfactorily designed, and that proper steps are taken to support the incipiently-formed crystals in the mother liquor, from which alone they can grow to satisfactory dimensions.

The essential considerations are to ensure an unvarying acidity of about 5 per cent H_2SO_4 , that the design of the distributing pipes and the velocity of the steam-ammonia stream passing through the perforations of such pipes are such as will adequately support the crystals, and that a time contact for growth, of the order of about one hour, is ensured.

By-product sulphate of ammonia made from pyrites or spent oxide acid has, as a nucleus, a quasi-alum (ferrous ammonium sulphate). With controlled development the crystals have a screen analysis as given below, and they invariably consist of combinations of three crystals (see Fig. 136),

Grist Characteristics of Sulphate of Ammonia

Remaining on	30 × 30 I.M.M. screen	. 78.67 per cent
Passing	50 × 50 I.M.M. screen	. 8.86 „
Passing	80 × 80 I.M.M. screen	. 2.33 „

These crystals are known as “dumb-bell” crystals, but for practical purposes the unsightly dumb-bell ends are avoided, and the crystals consist of the three symmetrical stems closely consolidated. Fig. 135 shows the drillability of Metro Sulphate crystals, as ordinarily supplied to the fertiliser trade, and Fig. 136 shows the dimensions of the crystals as fully developed.

Attention has recently been given to methods for improving the quality of by-product sulphate of ammonia at gasworks and coke-ovens, with a view to obtaining a hard crystal of satisfactory size, 3 : 1 length-to-breadth ratio, neutral and dry, and of satisfactory whiteness. When ammonium sulphate is crystallised in acid solutions containing small quantities of aluminium, chromium or ferric iron, slender thin crystals are formed, which are fragile. It is suggested that the addition of oxalic acid to the bath liquor of acidities ranging from 2½ to 8 per cent constitutes the simplest known method of obtaining control.

What should be remembered is that most saturators are unnecessarily large, and are not provided with suitable means for the support of the crystals in the mother liquor, from which alone they can grow, for a sufficient time. Given the correct dimensions and design of saturator,

and suitable control, it is an easy matter to prepare a satisfactory hard crystal of a size which is not fragile. With spent oxide acid of known quality there should be little need for the removal of the ferric iron as a complex ferrioxalate. Indeed, most saturators are operated under the reducing influence of H_2S , with the possibility of traces of SO_2 being retained in the sulphuric acid until it reaches the bath.

Concerning the suggestion that the drying of moist sulphate of ammonia was unnecessary, in that neutral ammonium sulphate absorbed moisture equally with acid sulphate of ammonia; it can be said that the suggestion in question is unfounded. It has to be remembered that atmospheric conditions might be such that actual deposition of water would occur. This deposition would vary in magnitude, both with the time during which the normal conditions prevail and with the relative humidity of the atmosphere. Indeed, it is found that generally speaking the absorption of moisture by sulphate of ammonia is closely related to the relative humidity, but that there is a material difference between the absorption of water by neutral and ordinary sulphate of ammonia.

Broadly speaking, with a relative humidity of 50 to 55 per cent neutral salt maintains its dry and drillable character, while ordinary sulphate of ammonia as low in acid content as 0.2 per cent H_2SO_4 contains as much as 0.1 to 0.2 per cent of water, which certainly renders the salt undrillable. The importance and necessity of drying are obvious.

The effect of the introduction to the fertiliser market of growing quantities of sulphate of ammonia of large crystal size, neutral, and practically bone dry, as just described, was to invite the question: could not something similar be done with calcium superphosphate and the various compound fertilisers supplied by the superphosphate manufacturers in order to overcome the "cakey" and sticky condition and to admit of much better drillability?

This leads by a natural sequence to the question of the granulation of various fertilisers and the processes which have been adopted for supplying many fertilisers in a granular form to meet the developing requirements of the fertiliser industry.

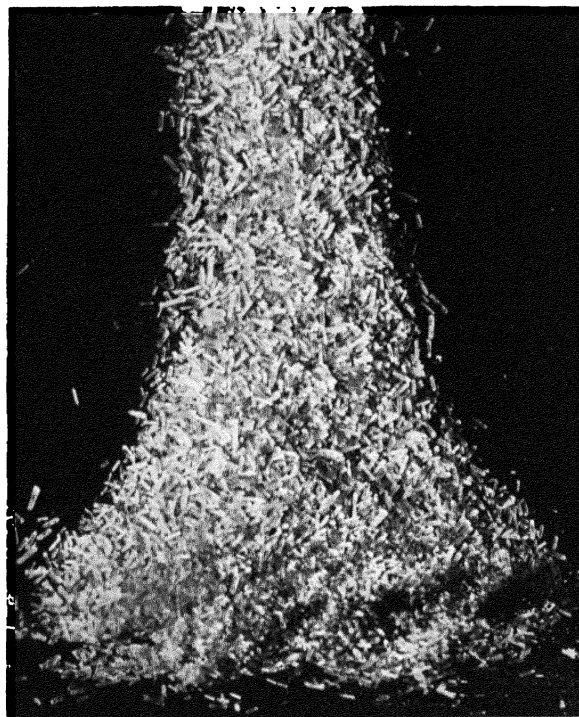


FIG. 135.—ILLUSTRATION OF THE DRILLABILITY OF METRO SULPHATE OF AMMONIA

Granulation

A granular material is one which has been formed into comparatively small particles of approximately uniform size, such particles being of such physical condition that they are not capable of being reduced by ordinary means to a smaller size, and indeed are not friable. Originally, of course, the material may be massed considerably larger in point of size than the product of the granulating process, or on the other hand, the material initially may be in the form of a fine powder.

Various methods are available for granulating a fertiliser, or fertiliser materials, and those appositely coming under this heading are: compressing, crystallising, flaking, graining, grinding, shredding, spraying and rotary drying.

By crystallisation one generally conceives that water is present, constituting part of the crystal, as in the case of alums crystallising with 24 molecules of water, or as in the case of copperas (iron sulphate), with seven molecules of water, or copper sulphate, with five molecules of water, or zinc sulphate, with seven molecules of water. But it should be remarked here that the ammonium sulphate crystals, as shown in Fig. 136, do not contain any water of crystallisation, but are in themselves true crystals, obeying the laws of crystallisation and are free from water of crystallisation, and practically free from any uncombined water.

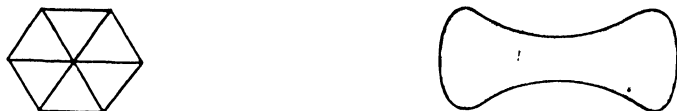


Fig. 136.—STRUCTURE OF FULLY DEVELOPED METRO SULPHATE CRYSTALS

With calcium superphosphate and compound fertilisers it is not a crystal that is sought, but rather a granule. Granulation is that process which results in converting a material into comparatively small uniform granules of irreducible size.

Physico-chemical principles underlying granulation of calcium superphosphate.—Den calcium superphosphate made in a normal way can be granulated by adding a small quantity of water (some processes do not require water, but involve the addition of phosphoric acid or mono-ammonium phosphate), agitating it at atmospheric pressure and temperature in a special form of equipment. No intermediate storing or maturing period is called for.

The excess moisture must be removed immediately following the granulating process by drying with heat at atmospheric pressure during the time that granulation is proceeding. The water content of the granules is of the order of $2\frac{1}{2}$ to 5 per cent, depending on the process.

Either an Eirich mixer or a rotating drum or conditioner can be used. More detailed reference will be made to the mechanical features later. The particle size of the granules of an agglomerated superphosphate arising at the discharge end of the mixer, or conditioner, is a function of the quantity of water added. The granulated material should remain in the store for three days to a week, during which period the nodules become very much harder, and have a crushing strength several times that of the fully-matured den superphosphate.

Any tendency to form "fines" in the final product can be counteracted by increasing the rate of feed of water: on the other hand, if any undue quantity of oversize is being produced the rate of addition of water is reduced.

The mechanism underlying this apparently simple process is intriguing. It may be explained thus. The free acid in calcium superphosphate is essentially and invariably phosphoric acid. Any sulphuric acid present is limited to a trace. Judicious and uniform wetting redistributes the phosphoric acid and may promote the hydrolysis of the monocalcium phosphate. Parenthetically, it can be said that where phosphoric acid is added there is obviously direct redistribution: where monocalcium phosphate is added, if this is in the form of a concentrated solution, there may be hydrolysis of this constituent.

On drying the phosphoric acid is concentrated, and this factor, aided by the influence of the elevated temperature in the dryer, facilitates the attack of the free phosphoric acid on the insoluble P_2O_5 . Strong phosphoric acid, in contra-distinction to sulphuric acid, resets more rapidly than dilute acid.

Drying the superphosphate after granulation improves the physical condition, and on storage admits of the hardening of the granules, so that they do not subsequently "cake," provided deposited moisture is avoided. In all cases it would appear desirable to maintain the temperature of the store above dew-point.

Features of the Granulating Apparatus.—The Eirich mixer was originally fabricated according to a German patent. It has a counter-current mixing pan, fitted with special tools, and it has proved peculiarly satisfactory for granulating all kinds of fertilisers. Eight to ten per cent by

weight of water is added. When the machine is employed for mixed fertilisers the mixing and granulation can be effected in one process. The time required is from three to four minutes. At one large works the Eirich mixer is used for the preparation of a granulated mixed fertiliser, the various components being initially mixed, then phosphoric acid is added, and after the reaction, the granulation is effected by the addition of water. All four unit processes—mixing, addition of acid, reaction and granulation—are effected without interruption in one machine, whereas hitherto the materials were first mixed in a drum mixer, charged into large stirring vessels for the addition of the phosphoric acid and reaction, and subsequently granulated in a further complicated machine.

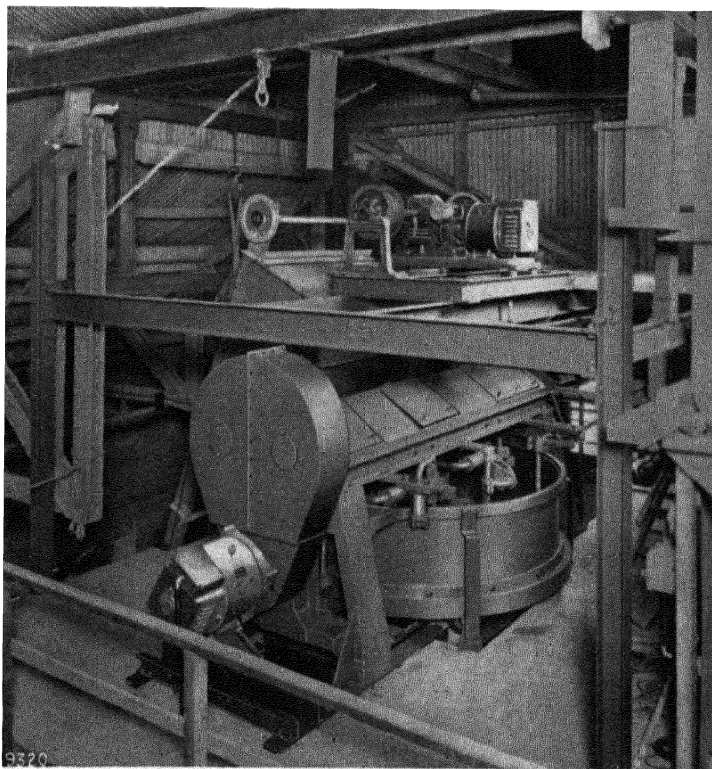


FIG. 137—EIRICH MIXER.

The size of the granules can be regulated by controlling (a) the mixing speed, (b) the amount of water added and (c) the temperature of mixing. The outputs obtainable with various sizes of Eirich mixer are as follows :—

5 cubic feet size	..	about 16 to 20 cwt. per hour
9 " " "	..	" 2 tons "
18 to 20 " " "	..	" 4 to 5 tons "
36 to 40 " " "	..	" 8 to 10 tons "

To afford some further indication of the features and value of the Eirich mixer it can be said that the mixing arrangement consists of an open or enclosed type of pan, rotating on four trunnion wheels, which feeds the batch continuously to the mixing stars revolving in the opposite direction. The mixing star is eccentric to the pan, and is provided with a number of spring-mounted manganese steel blades placed in such a manner as to give the maximum number of points of intersection during its travel, as clearly shown by Fig. 138.

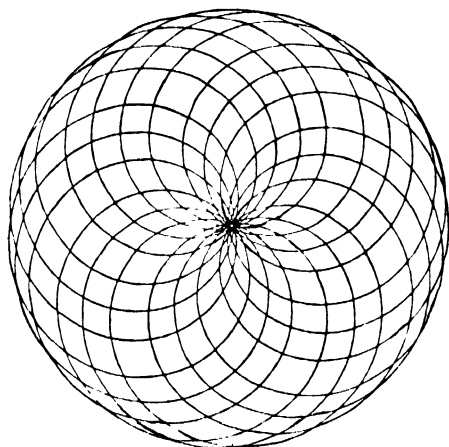


FIG. 138A.—DIAGRAM SHOWING CURVES FROM ONE MIXING BLADE IN DOUBLE-ACTING COUNTER-CURRENT (EIRICH) RAPID MIXER

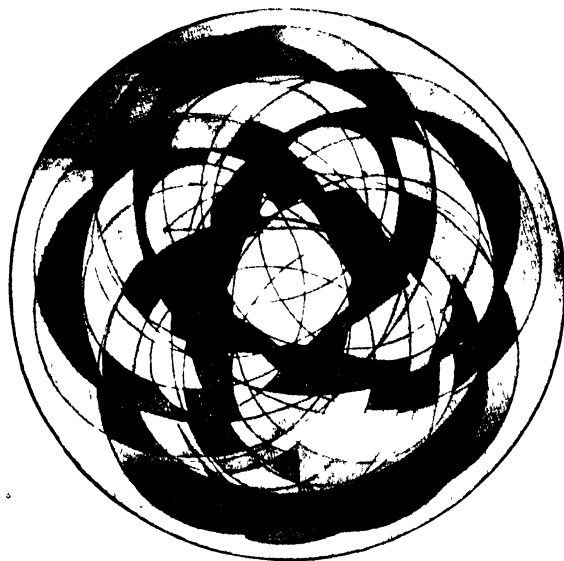


FIG. 138B.—CURVES SHOWING MOVEMENT OF ROLLER AND BLADES DURING ONE REVOLUTION OF AN EIRICH PAN

Owing to the rapid circulation, even the most difficult raw materials are intimately and evenly mixed in a few seconds. The speed of the pan, in relation to the speed of the mixing star, is 1 to 5, dependent upon the composition of the batch, the layer ranges from 2 inches to 10 inches high, and the action of the pan results in an even layer being maintained.

The counter-current effect produced by the pan and mixing star results in a unique multiform.

The thin layer of material in the pan is carried, by the counter-current action, at a moderate speed towards the quickly rotating mixing star. Fig. 139 shows that at the points of intersection of both movements and at the periphery of the mixing blades the batch materials are turned on vertical axes.

The effect is considerably increased by the vertical side scraper and corner blades, which are stationary, thereby forcing the batch into and through the narrow passages. This turning movement lifts the batch into waves ranging from 2 inches to 10 inches high, which in turn are carried again into the streams created by the pan and stars. A similar valuable movement is created in the mix at the cutting points at the periphery of the pan and mixing star. The combined action ensures that every grain of material is turned over and brought from the bottom layer to the top surface and *vice versa*. In this way the whole batch is maintained in a constant state of agitation.

The mixing blades are fixed at an angle which ensures that in addition to the stirring action, they force the batch upwards and over by the movement of the pan, and so assist in breaking up and distributing the aggregate (see Fig. 140). Here again the counter-current action greatly assists

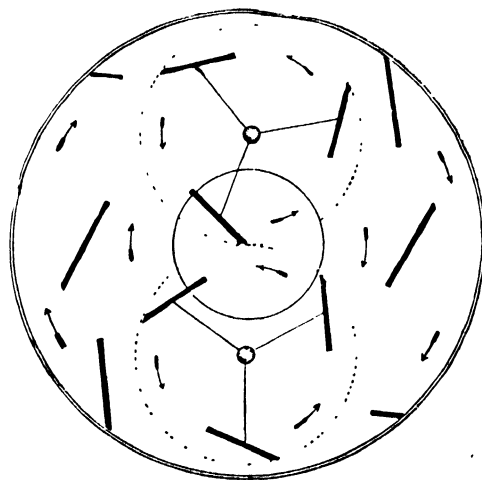


FIG. 139.—DOUBLE-STAR EIRICH TYPE MIXER



FIG. 140.—DIAGRAM SHOWING THE FORCING UPWARDS AND OVER OF AGGREGATE IN AN EIRICH PAN

in turning the particles over in the direction of the star movement. It will, therefore, be seen that the mixing tools of the star have a moving, loosening and distributing action, whereas the stationary side scrapers and corner blades both have the reactionary effect of consolidating and accelerating the mixing.

The innumerable movements, diversity of paths and intersecting points applied to every particle of the mass are unique features of the Eirich mixer.

Application of Granulating Processes to Existing Works

There are three types of granulating plants now in use. Local conditions, which are referred to below, determine the most suitable plant to adopt.

If a continuous superphosphate den already exists, the granulating process can be incorporated to work continuously with the den. The layout is shown in Fig. 141. The superphosphate, as it is discharged from the den "A" falls on to a steel tray or belt conveyor "C". If it is superphosphate only which is being granulated, the process continues as follows:—

The conveyor delivers the superphosphate to a special type of pulveriser "D," and from there it is elevated to a rotary conditioner or granulator, "E." In this machine water is added, either cold or hot. The water is under accurate control by means of regulating devices. Here the granules are formed, and they will be of varying size, depending on the amount of liquid used. They gravitate to a rotary dryer-hardener, "G," and the time they are retained in this machine determines the hardness of the granules. When they are discharged the moisture content should be from 4 to 6 per cent. The granulated product is then passed to a cooler, "H," of the horizontal cylindrical type, where a large volume of atmospheric air is continually circulating.

The temperature of the granules leaving the cooler should be approximately only 15° F. above atmospheric temperature, and it should never exceed 90° F. Cooling militates against subsequent setting in the pile or in the bags. In fact, in the absence of cooling the product cannot be bagged direct. After cooling the product is again elevated to a screening plant, "I," where it is divided into three grades, *viz.*, oversize, usable product and fines. The oversize is passed to a specially designed pulveriser, "J," which reduces the large granules to the usable size, with a minimum of dust.

Before returning the pulverised product to the screening unit, it is necessary to re-circulate it through the cooler. The reason for this is that the large granules may not be dry in the centre, and the crushed product would tend to block the screen. By circulating through the cooler first, the product is more completely dried and the damp core removed. The fines extracted by the screen are automatically returned to the granulator.

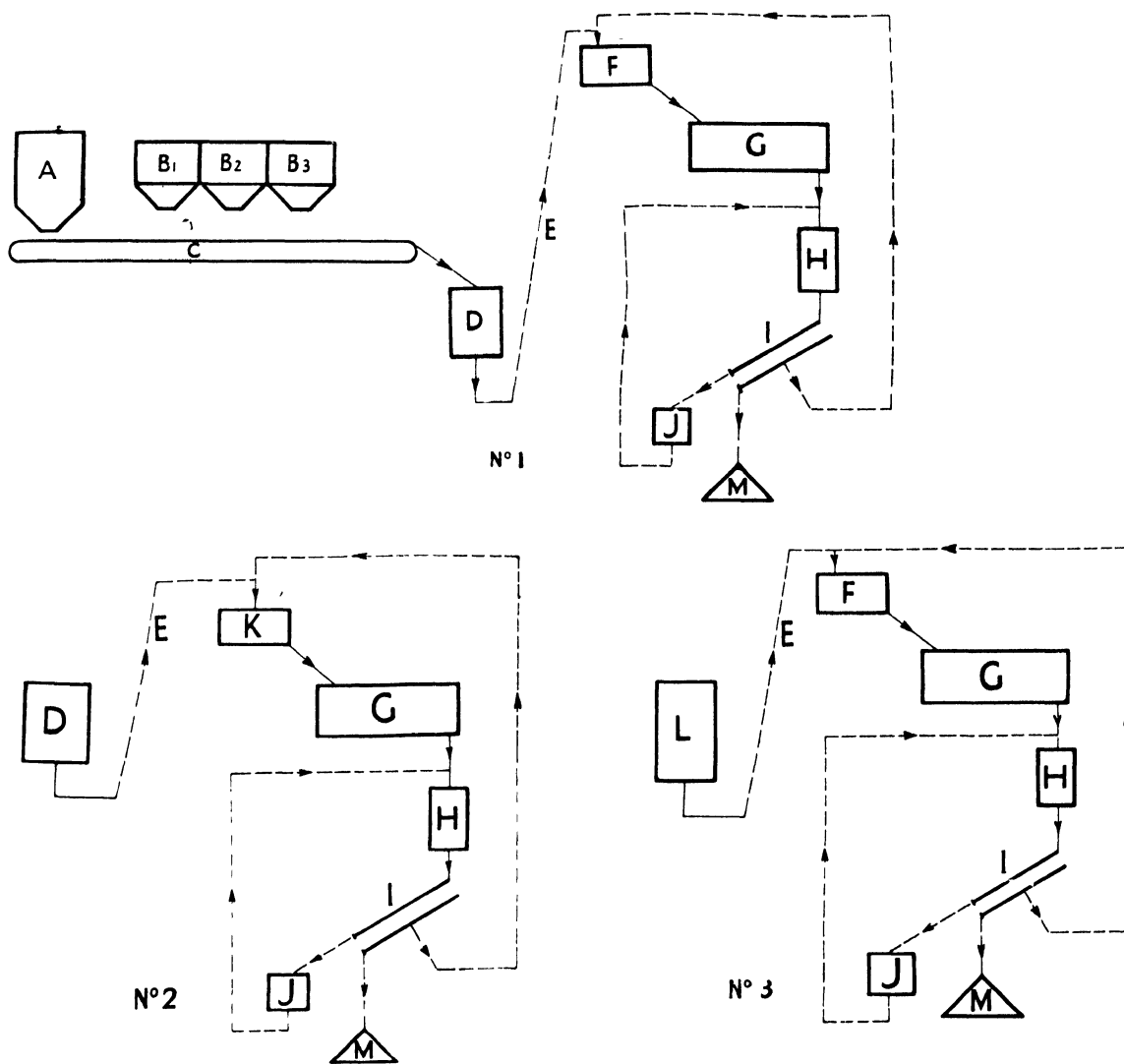


FIG 141 —THREE TYPES OF GRANULATING PLANT.

This same layout can be used to granulate compound manures. Referring again to type "1": three hoppers are shown, B₁, B₂ and B₃. These are kept filled with the ingredients to be added, such as sulphate of ammonia, potash and filler: any number of hoppers can be arranged, to suit the ingredients to be used. Underneath each hopper there is an automatic feeder of the belt or electric vibrating type. These are set to deliver the correct amount of each ingredient to correspond with the flow of superphosphate from the continuous den, and can be relied upon to give the correct analysis.

Type "2" represents another type of plant and is applicable where superphosphate is taken from the floor after maturing.

The materials to be compounded are weighed in batches: this can be done mechanically, as described later. It can also be undertaken manually if the output does not warrant complete mechanical handling.

The batch is usually 10 cwt., but it may be as large as 1 ton. The skip bucket is elevated and the contents tipped into an Eirich granulating mixer "K." This machine, which has been described already in full detail, ensures thorough mixing of the ingredients, and aided by the addition

of water, the action of the stirrers causes the granules to form. Up to this point the process is a batch one, but thereafter it becomes continuous. The mixer discharges its batch of wet granulated material into a hopper of special design. Underneath the hopper there is a belt conveyor which regulates the flow from the hopper to correspond with the hourly capacity of the plant. From this point the process is exactly the same as in type "1."

Type "3" shows a plant similar to that illustrated by type "1," as far as the actual granulation is concerned. It is designed to work with an up-to-date batch mixing plant, which may already exist.

Letter "L," type "3," represents the mixing unit. In a 5-tons per hour granulating plant, batches of 1 ton of mixed compound manure are delivered from the plant every 12 minutes. These batches are elevated to a storage hopper. Below the hopper there is a smoothing-out belt conveyor, which withdraws the product at a pre-determined rate to suit the capacity of the granulating plant, as mentioned above. The conveyor delivers to the rotary granulator "F," and from this point the plant is exactly similar to that described in type "1."

In these granulating plants the noxious gases containing hydrofluosilicic acid are withdrawn from the dryer-hardener and the cooler. These gases cannot be exhausted to the atmosphere. They are first drawn through cyclones, where the dust entrained by the gases is settled out and then pass to a series of wash towers, fitted with fine water sprays, which remove all traces of acidity and admit of compliance with the Alkali Act.

Comparisons of the two systems, i.e., Eirich and rotary granulator, may be of interest.

In the Eirich mixer plant it is practically impossible to keep the proportion of fines (below 1 mm.) less than 25 per cent of the output of the requisite size granules, *viz.*, 1 to 4 mm. This is a handicap, as the fines, if returned to the process, require more water to re-granulate, and thus increase the work of the dryer.

In the rotary granulator the proportion of fines rarely exceeds 8 to 10 per cent, which is a distinct advantage.

The granule produced by the rotary system is a more perfect sphere and is harder than that produced in the Eirich mixer with an equal moisture content. In consequence, to get granules to withstand the pressure of storage, by the Eirich system the moisture has to be reduced to approximately $2\frac{1}{2}$ to 3 per cent, whereas granules produced in a rotary system may have 4 to 6 per cent of moisture and yet withstand the pressure of storage. This distinctive feature of the granule prepared by the rotary method allows of an economy of fuel, and moreover, less power is required to produce it.

The following figures are taken from plants of equal capacity per hour.

Eirich system . . . 13.5 electrical units per ton output.

Rotary system. . . 8.9 electrical units per ton output.

The process of granulation does not add to the cost of manufacture compared with the older method of compounding, if all the factors are taken into consideration.

There is a decided saving in labour, because granulating plants can be made automatic throughout. There is no maturing period, with the subsequent breaking down and re-dressing, as is the case with the compounding method. If the granules are cooled sufficiently they can be bagged direct from the plant and stored without detriment.

The following are approximate figures for granulation, based on actual cost data supplied to the authors. They are governed to some extent by local conditions and the layout of the works.

	5 ton per hour unit.	
	s	d.
Coal, 150 lb. at 47s. per ton		8
Electric power, 65 electrical units at 1d.	1	1
Water for granulating and washing the gases: 500 gallons at 1s. 3d. per 1,000 gals., say		2
Labour to operate, excluding manual feeding and bagging off: 2 men at 2s. per hour		10
Wear and tear		9
Depreciation, 10 per cent on capital outlay, based on 20,000 tons per annum	1	0
		<hr/>
		4 6
		<hr/>

It has been found that certain ingredients act as binders, reducing the amount of dust which is entrained during granulation. The plant output increases in proportion to the extent to which entrainment of dust is avoided. Whatever binding ingredient is used, it must be relatively cheap, as it possesses no fertilising value. An addition of 2 per cent of any one of the following ingredients may be used to advantage.

- | | |
|----------------|-------------------|
| Bentonite. | Gypsum. |
| Dextrine. | Ground phosphate. |
| Farina flour. | Kaolin. |
| Fullers earth. | Kieselguhr. |
| | Potato flour. |

Some of these binding agents have a tendency to preserve the original size of the granules, if the bagged material is exposed to humid atmospheric conditions. But it is becoming more and more apparent, since the introduction of granulated manures, that this product must be stored under reasonable conditions, otherwise setting will take place, either in the pile or in the bags. These high-class manures should be stored in buildings where hot air of 65° F is circulated, in order to avoid the deposition of dew.

To overcome the tendency to "set," manufacturers at present are experimenting with paper sacks having a bitumastic lining. Farmers are not partial to handling this type of sack. A store maintained under the conditions already indicated is the only certain method of ensuring the delivery of a product to the farmers' lorries that is calculated to give unqualified approval.

Fig. 142 represents the layout of a granulating unit embodying an Eirich mixer, and has a capacity of 5 tons per hour. In this plant there are a series of batching hoppers shown, six in all. These are kept filled with the various ingredients by means of an Eclipse or Chaseside mechanical

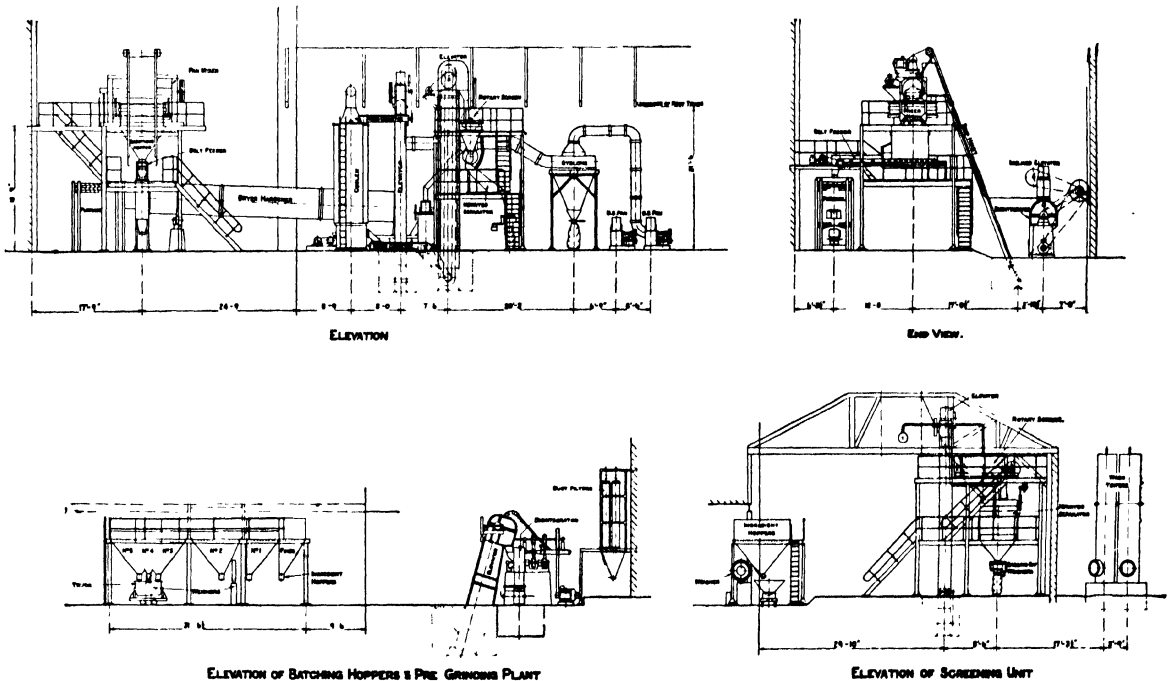


FIG. 142.—LAYOUT OF A GRANULATING PLANT EMBODYING AN EIRICH MIXER

shovel. The former is shown in Fig. 117. Underneath the hoppers there is a Decauville track with side-tipping wagon. At two points along the track there are steelyard weighers with the recording dials facing the line of travel.

One man operates the truck and withdraws from the hoppers quantities of the different ingredients to be used in the batch. Fig. 143 shows a Chaseside shovel charging a series of batching hoppers: the large-scale dial is also visible.

Fig. 144 shows a granulating unit embodying a rotary conditioner: the bagging-off points are in the foreground.

Fig. 145 is a view of an Eirich mixer with the skip hoist winding gear situated overhead, and smoothing-out conveyor to dryer.

Size of Granule—There is still no agreement about the most suitable size of granule to be produced. In the early stages of the process it was assumed that the granules would vary between $1\frac{1}{2}$ and 4 mm. During the war period, when fertiliser factories were urged to produce the maximum output, those works which were producing granulated compounds immediately ceased to extract the dust. Thus, the farmers were supplied with granules varying from 4mm. down to dust, the portion below $1\frac{1}{4}$ mm. approximating to from 15 to 20 per cent. The farmers generally are pleased with the product, as it is suitable for use in the combined drill. So long as they do not press for a more regular product the practice will continue. But ultimately the manufacturer will be compelled to remove the dust, as uniformity of granules is a desideratum.

On the other hand, certain agriculturalists advocate two grades of granules, one for use at seed-time, the other later. They favour granules between 4.5 mm. and 2.5 mm., and for later application between 2.5 mm. and 1.0 mm. The manufacturer will be able to meet any demand that may be imposed, as differential screening is all that is involved.

It is more than likely that the ultimate size which will suit all conditions will be a product varying from 1.0 mm. to 4 mm.

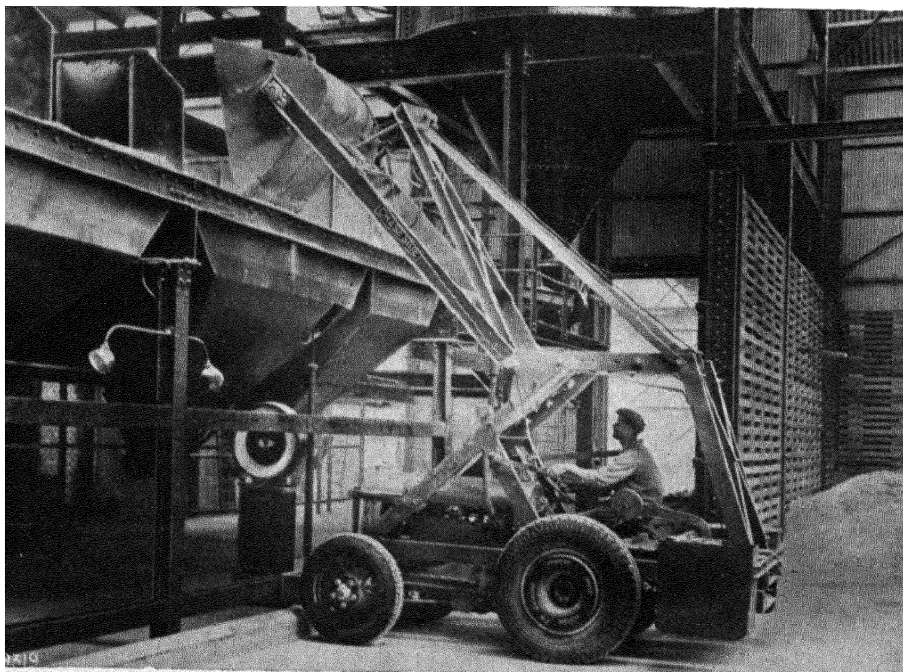


Fig. 143.—BATCHING HOPPERS OF COMPOUND MANURE GRANULATING PLANT

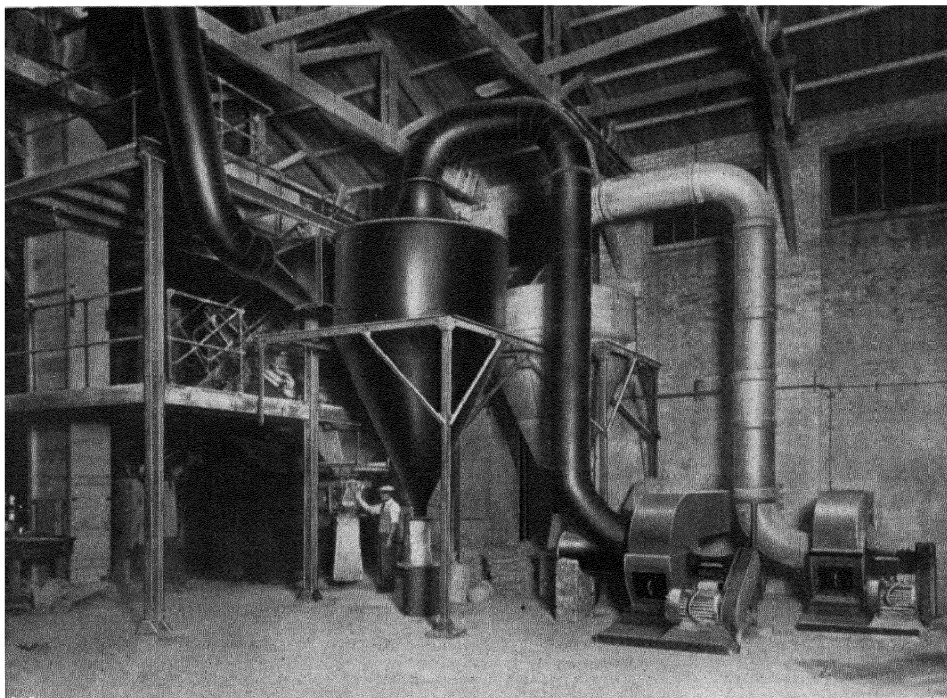


FIG. 144 -BAGGING-OFF POINT AND DRAUGHTING EQUIPMENT ON GRANULATING PLANT

Apart from what has been referred to, reference can appropriately be made here to processes evolved since the question of granulation assumed importance in 1936-1938.

Nordengren furnished the authors in 1938 with particulars of his process. The superphosphate is taken as it emerges from the den at the highest temperature possible. The product is introduced to a mixer, where it is worked in a certain way, and granules are formed without any addition. Newly-made superphosphate easily forms granules, and the sizes of these can be influenced by regulating the mixing tools and their velocity in the mixer. The granules formed are at first quite soft. They are passed into a revolving drum, in which they are rolled without heating for about 40 minutes. This process hardens the granules. The product is screened, the larger lumps are crushed and the smaller particles returned to the mixer. The process is practically continuous and only the mixing is intermittent.

This process does not adversely influence the solubility of the phosphoric acid, and the yield is quite the same as with ordinary superphosphate. The fraction taken out as marketable product has a particle size of 1.6—3.5 mm. If stored, these particles may lightly clog together, but with the least movement such a cluster of granules is readily separated. The process is protected by patent rights. The advantage of the foregoing process lies in the fact that no addition of water is required and thus there is a saving of fuel as contrasted with most of the other processes.

Although singularly little superphosphate as such has been put on the market in Europe in a granular form, quite a large part of the production in the United States is being granulated. Physically, the granular product differs very much from the ordinary superphosphate. It is more easily bagged, and if jute bags are smeared inside with hydrated lime there is no corrosion, as occurs with the finely-ground product. Distribution on the fields is easier to perform, and the product is more evenly spread. Field tests undertaken in Sweden show that a granular product gives much better results than ordinary superphosphate on all soils, but especially on those with an acid reaction, such soil being generally poor in phosphate. There is reason to believe that the superphosphate of the future will be manufactured in a granular form. Such superphosphate will doubtless be produced continuously, and granulation will be effected as part of such continuous process.

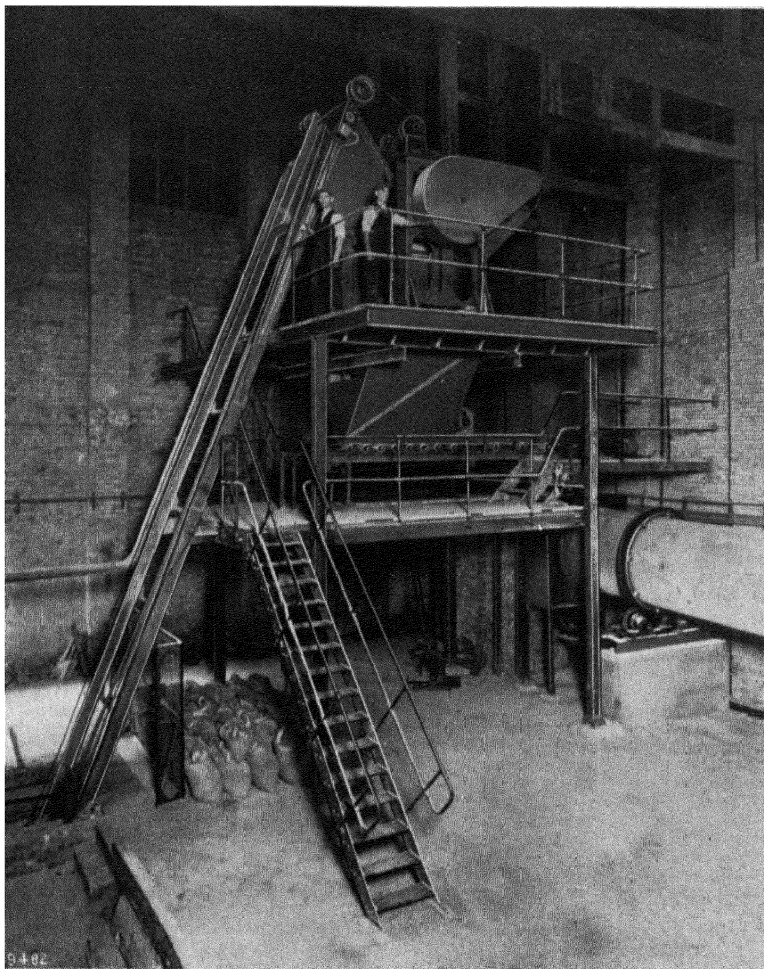


FIG. 145 GRANULATING PLANT WITH EIRICH MIXER SHOWING SKIP HOIST AND SMOOTHING-OUT CONVEYOR

The process of A/B Kemiska Patenten can also be used for the production of granular compound manures containing superphosphate, in which case the fresh superphosphate is mixed with the other ingredients. If necessary, a small quantity of water may be added. The apparatus is the same as for ordinary superphosphate, and consists of a mixer, a revolving drum, a screening apparatus and a crusher, together with the necessary elevators and other means of transport.

Parrish and Ogilvie.—This process is one which contemplates the addition of two of the constituents of a three-element-containing fertiliser as a magma to the other which is in course of preparation.

For example, a magma of sulphate of potash, sulphate of ammonia and sulphuric acid is added with the acid feed to the phosphate rock to a special mixer, in order that a three-element-containing fertiliser is obtained, in a form that admits of granulation in a conditioner, after which it is dried in a rotary dryer. The products of combustion are introduced at the inlet end with the compound fertiliser, in order that a uni-directional flow is obtained.

By a "three-element-containing fertiliser" is implied one having nitrogen, P_2O_5 (phosphate) and K_2O (potash) as the essential constituents.

Another possibility with this method is to add a sulphuric acid-containing sulphate of potash in solution to phosphate rock, and to neutralise the excess acid with liquor ammonia of 25 per cent NH_3 . This method is flexible, and allows one to secure uniform distribution and/or production

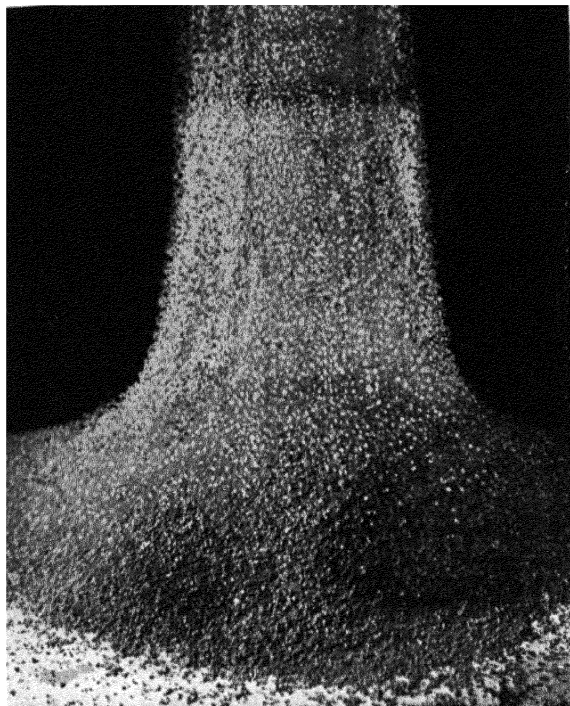


Fig. 146.—F.P.P. GRANULAR FERTILISER

form of a slurry, is then passed to a rotating granulator or conditioner, in which further moisture can, if necessary, be added by spraying with water. The granulated product is passed to a dryer for final hardening.

Other fertiliser constituents such as sulphate of ammonia and potash salts, finely ground, can be added to the granulator to produce compound granular fertilisers.

From the above description it will be seen that the Procter process simplifies the procedure in fertiliser works practice.

It has, however, been suggested that the Procter process does not give a high yield of water-soluble P_2O_5 from the phosphate rock used, and a still less satisfactory yield of water-soluble P_2O_5 when compound fertilisers are manufactured. Whether this is due to the fact that the rock phosphate is not sufficiently finely ground, whether it is a question of failing to use a weaker sulphuric acid, whether it is due to the absence of intimacy of mixing, or whether it is attributable to inadequate time contact, is at present unknown. All these factors appear to call for systematic examination. What is impressive is that the Procter process gives an attractive granular product, and because of this, any suspected weaknesses will doubtless be fully investigated.

As previously indicated, during the drying process there is a chemical reaction, the undecomposed phosphates of the superphosphate being attacked by phosphoric acid. The products of combustion are thus associated with toxic gases and moreover, they entrain dust. In two of the larger granulating plants working in this country, Holmes-Jaffhor rotor dust extractors have been installed to remove the dust, etc.

The Holmes-Jaffhor Rotor Dust Extractor consists essentially of a casing in which a drum, or rotor, built up of small strips, is revolving at a suitable velocity. Figs. 147 and 148 show views of the extractor, and are largely self-explanatory. The drum revolves in the direction of the incoming gas, causing the gas adjacent to the drum to revolve at the speed of the drum, i.e., an annular layer of gas remains stationary in relation to the rotor, but revolves in the casing. The dust particles in the gas are carried within this inner zone by the centrifugal force, and fall into the hopper provided underneath the rotor, while the clean gas is drawn into the body of the rotor

throughout the mass. Operating in such a way, and using a special form of mixer, some of the difficulties attending the physical compounding and formation of granular fertilisers can be obviated. This is largely attributable to the fact that better distribution of the phosphoric acid is attained than is possible by a method relying on distribution of the phosphoric acid secured *via* wet-spraying.

Procter Process.—There is another process in use which is likely to compete with other processes when further developments and improvements have been tried out. It is known as the Procter process, and is covered by patent No. 559,482.

J. T. Procter is one of the Directors of Hy. Richardson & Co. (York) Ltd., and has been working on this invention since 1940. The Sturtevant Engineering Co. Ltd. have collaborated with him in his experiments and are associated with him in the patent.

The process may be described as follows:—

Finely ground phosphate rock is treated in a special mixer with sulphuric acid in such quantity and under such conditions as to ensure chemical reaction between the rock and the acid. The superphosphate, in the

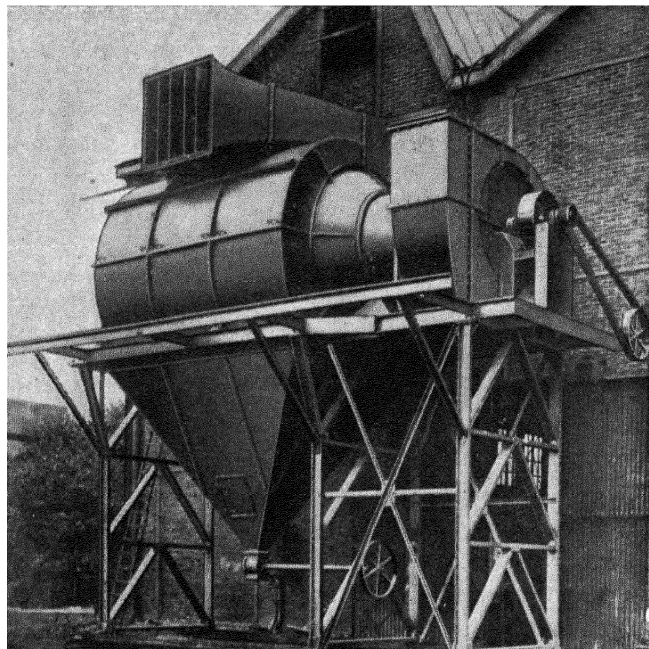


FIG. 147.—HOLMES-JAFFHOR ROTOR DUST EXTRACTOR

by means of the exhaust fan. The centrifugal force can be varied by the speed of the rotor, according to the fineness of the particular dust to be removed, the withdrawal of the finer dust requiring a higher rotor speed.

Any fine particles not arrested by the extractor pass to a scrubber, which is provided on the outlet of the extractor, essentially with a view to dissolving the toxic gases, and thus meeting the requirements of the Alkali Act.

Reference has been made in this chapter to bag-rot, and the cementing of granular fertilisers in the bags, particularly when large quantities are accumulated in the store and there is a super-imposed weight. It is felt, however, that this aspect should be further emphasised.

Granulated N.P.K. fertilisers, in the opinion of the authors, should be made alkaline, that is, they should have a pH value of not less than 8.0–8.5. Apart from this, the material leaving the granulator should be cooled by the passage through a tower or rotary cylinder of an adequate quantity of dry air. The granular fertiliser should be cooled to say 25–30° C. before bagging.

Bag-rot largely arises from the free phosphoric acid, or from phosphoric acid reacting with muriate of potash and undecomposed fluorides, thus slowly evolving hydrochloric and hydrofluoric acids. To arrest this reaction the authors suggest the need for making a slightly alkaline granulated N.P.K. fertiliser. If the ingredients, during mixing and prior to granulation, are given a pH value of 8.0–8.5 there is reason to believe that the evolution of hydrochloric and hydrofluoric acids will be obviated, and that bag-rot will be reduced to a minimum.

Meanwhile, fertiliser manufacturers have under contemplation the use of paper liners with bitumen interspersed between the plies, for the present type of granular fertilisers. The paper liners in question hitherto have been used to render the fertiliser bags waterproof, but they may well prove to be suitable to protect the hessian or Calcutta twill, or whatever is used as the outer bag. If objection is taken to paper bags, then the hessian, or Calcutta twill, or whatever is the substance of the bag, should be given a protective impregnation of bitumen or other suitable protective agent.

A view of the granular compound fertiliser manufactured by Messrs. Fisons, Ltd., Ipswich, is afforded by Fig. 146, which incidentally shows its drillability.

An indication of the cost of granulating superphosphate is bound to be of interest. Mr. Nordengren, in a communication to one of the authors, has remarked :

“We have had no difficulty in granulating superphosphate with normal percentages of free phosphoric acid. We are building a plant here—capacity about 60 tons per day. We are not yet in a position to give definite figures regarding production costs, but believe the power necessary will be about 50 h.p., and that one man in 8 hours will be able to work the plant. No heat is required, and repairs, in all probability, will be low. There is no reason to believe that the costs will be very high. It is expected that approximately 6d. per ton will cover the costs.”

That compound fertilisers in a granular form will be more expensive to produce than granular calcium superphosphate is clear. To secure a homogeneous product constituted of three fertiliser elements in the form of granules necessarily means grinding. It has been found, as has already been referred to, that experiments have demonstrated that it is necessary to grind to about 200 mesh, in order to get a mixture of three dissimilar fertiliser elements, say calcium superphosphate, sulphate of ammonia, and sulphate of potash, of reasonably uniform chemical composition. To attain this ideal condition before granulating may not be essential, but something approaching this state of fineness of the three constituent elements of a compound fertiliser may have to be approached, if the granules are to be of strictly identical composition.

Another condition to be sought is uniformity of size of granules, and this necessarily implies that a sensible quantity of both under-size and over-size material has to be rejected by the screens. All this costs money.

The following statement may be regarded as approximately correct, as representing the cost of the granulation of compound fertilisers in 1938 :

	Cost per ton.
	s. d.
(a) Cost of grinding the constituents of the compound fertiliser	6
(b) Electric power : 12·5 kw. per ton, at 1d. per kw. hr.	1 0½
(c) Labour : one hour per ton of granular product produced	1 3
(d) Fuel : say ¼ cwt. per ton of granular product, at 20s. per ton	3
(e) Repairs and maintenance, lighting, heating, insurances, rates, and taxes, interest on capital at 5 per cent, depreciation at 7½ per cent : say 25 per cent in all.	
Approximate cost of plant embodying three special granulators (two working—one as a spare) : granulators work for 16 hours per day, for 200 days per year, at a capacity of 10 tons per hour each granulator : production, say 64,000 tons per year :	
Cost of complete plant, say	£15,000
Cost of buildings	5,000
	£20,000
	£20,000
25 per cent of £20,000 = £5,000	
= 100,000s.	
64,000 tons	1 7
Cost per ton	4 7½

That farmers should be in a position to meet this expense is certain, as the increased efficiency of application to the soil by the use of a granular fertiliser, as contrasted with the old type of product, must be at least 5 to 7½ per cent.

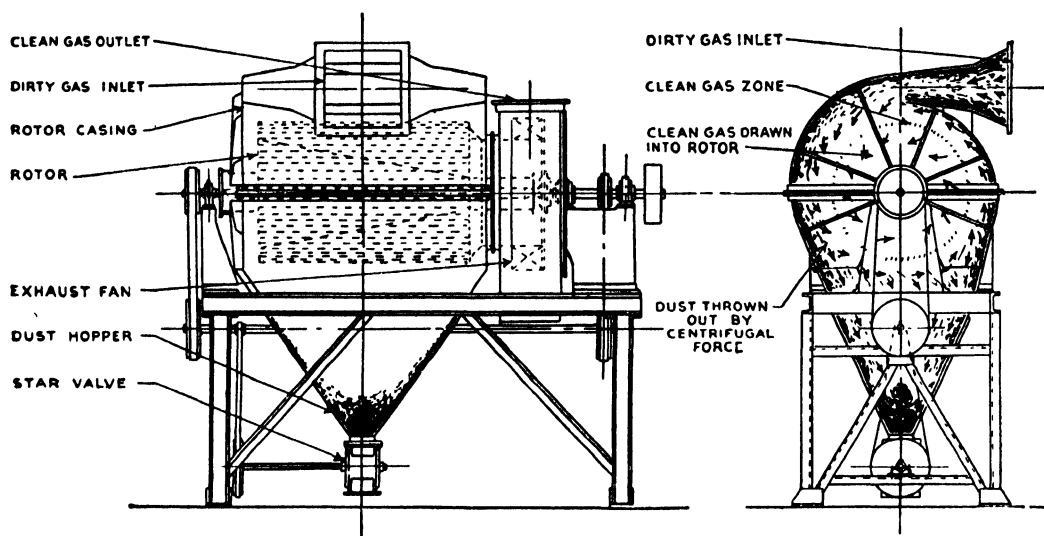


FIG. 148.—SECTIONAL VIEWS OF HOLMES-JAFFHOR ROTOR DUST EXTRACTOR

Taking the least expensive granular compound fertiliser, constituted of say 3.5 per ammonia, 21 per cent water-soluble phosphate, and 3 per cent potash (K_2O) the cost in 1938 was .

	Per ton.		
	£	s	d.
3.5 units of ammonia at 6s. 6d. per unit	1	2	9
21.0 units of w.s. phosphate : 9.6 units of P_2O_5 at 4s. per unit of P_2O_5	1	18	5
3 units of potash (K_2O) at 5s. per unit		15	0
	<hr/>		
	3	16	2
Cost of bags and string		5	6
Cost of packing		2	0
Average carriage charge to farmers, say		7	6
Cost of granulating, selling expenses, engineering, and manufacturing oncosts and overhead charges, say	1	6	4
	<hr/>		
Cost per ton	5	17	6

Assuming 5 per cent extra efficiency is derived by the use of granular fertilisers, it is obvious that the farmer can afford to purchase compound fertilisers in granular form. But the advantage to be derived from the use of granular compound fertilisers may well prove to be more than 5 to 7½ per cent, which has been indicated.

The authors have examined certain figures relating to investigations which have been made as to the extent to which calcium superphosphate and compound fertilisers are rendered available to the soil. The figures are alarmingly low, and it is known that in the case of granulated superphosphate, as contrasted with ordinary superphosphate, almost double the efficiency accrued. If results of this order can be demonstrated in the case of granular compound fertilisers, an incentive to their use will be immediately given.

One of the aspects on which fertiliser manufacturers should concentrate in the future is to undertake research, either through Rothamsted or some other investigatory station, directed to determining the efficiency of application of various fertilisers to various soils. A peaty soil may well retain solutions of soluble fertilisers, and render these available to the root crops or cereals, or whatever is under cultivation. On the other hand, a sandy, porous soil may admit of percolation of these solutions of soluble fertilisers outside the region of availability.

There may be reactions with constituents of the soil, which tend to reduce the effectiveness of the solutions in question. Many aspects surround the question of the efficiency of application of fertilisers, and it is obviously a subject which should be investigated, in the interests alike of farmers and fertiliser manufacturers.

CHAPTER XVIII

STRUCTURE OF THE BRITISH SUPERPHOSPHATE INDUSTRY, AND THE DESIGN AND MANAGEMENT OF A CALCIUM SUPERPHOSPHATE WORKS

THE fertiliser industry must organise itself, and seek representation where its views can be urged with clarity and understanding. Singularly few politicians know much about the agricultural industry, its allied activities and its needs: or how it can be soundly established in the economy of the nation. As to its importance, we need only recall what Mr. Lloyd George truly remarked in 1937. He said: ". . . The front where we nearly broke down in the Great War was the food front: it was food shortage which broke down Germany, Austria, Bulgaria, and Russia. It nearly broke us down before they broke down."

But the World War of 1939-1945 has emphasised even more sharply than the war of 1914-1918 how important is a vigorous and healthy agricultural industry to the existence of this country. Doubtless Mr. Churchill displayed greater agricultural wisdom than he himself realised when he asked farmers to plan for the period of 1941-44. During these years there has been a call for the ploughing of more land, so that cereals and root crops should be grown in ever increasing abundance. Arable acreage has increased by over 1,000,000 acres, and the total over pre-war has reached nearly 5,000,000 acres in arable and 4,500,000 acres in tillage area. Instead of production of crops for direct human consumption, the primary concern now is to increase production of livestock and livestock products. Prior to the war the total value of the output of British farming, including the farmers' own consumption and subsidies, amounted roughly to £290,000,000 annually. In 1942-43 the sum of £530,000,000 had been reached.

Good farming is something more than 100 per cent productivity. A set of values is implicit in it, which are not satisfied by mechanically ploughing six furrows at once, where our forefathers ploughed one, or by combining self-binding with threshing machines, in a simultaneous operation. Is the land, and all that it implies, to be saved by more and more machines? Is not farming a craft? Once a craft is mechanised, it is proved that it dies. It may be urged that such issues are irrelevant to the scientific agriculturalist, but is not Prof. Stapledon a scientific agriculturalist? In his book about "The Land" one will find perceptions deeper and intimations richer than the purely scientific attitude.

While circumstances have conspired to concentrate power and decision in the British fertiliser industry—particularly the superphosphate and nitrogen sections—in the hands of a few individuals, one cannot be certain that this concentration of power will continue indefinitely. There is much uncertainty at the present time as to the trend of political development. The whole political complexion of the country might well be changed within the next few months, due to circumstances which have come to light as regards the methods adopted in the representation of certain constituencies.

This was written in 1939, in our first edition. What we foresaw has now happened, namely, in 1945 a change of Government.

The superphosphate industry has never made extortionate profits: indeed, it has not been too easy to pay dividends of 5 to 7 per cent per annum on the ordinary shares. Such dividends are not unreasonable, in view of the risks that have to be taken and the general uncertainty which exists in this industry. Our earlier observations were made in prophetic vein, in much the same way that our original and somewhat similar chapter was conceived. On that occasion we foreshadowed in a remarkable way the direction in which the superphosphate industry would re-model itself, in order to ensure its future preservation. Our predictions have not been wide of the mark on two occasions: we may be correct in what we envisage in this chapter, namely, the need for a more intimate association with the gas industry.

Conditions in the superphosphate industry to-day are dissimilar to what they were in 1926 when our prophecy was made. No one will be inclined to deny that a metamorphosis has been wrought in the structure of the industry. What we remarked in 1926 was as follows:

¹ *Artificial Fertilisers, Their Chemistry, Manufacture and Application.* (Parrish & Ogilvie, Benn, 1927).

“ . . . With few exceptions superphosphate factories in this country are too small. Few are capable of producing more than 50,000 tons at one works. Many produce less than 10,000 tons. It can be affirmed that mass production as a result of modern plant and equipment, combined with cheap transit charges, will undoubtedly be the salvation of the British superphosphate industry.”

Further, we proceeded to observe :

“There must be amalgamation of works on the lines of the Interessen Gemeinschaft A.-G. of Germany—the inefficient works must cease to manufacture, and production must be concentrated at the works which are best adapted to manufacture the best product at the least cost. In connection with any such reorganisation of the industry, the proximity of the works to agricultural districts, and the railway rates applying for the several works in relation to the point of demand, must necessarily be carefully considered.”

LIST OF COMPANIES IN THE FERTILISER INDUSTRY IN THE BRITISH ISLES

As is now known, instead of there being a large number of small superphosphate works manufacturing ten to twenty thousand tons of products per year, Messrs. Fisons, Ltd. have absorbed many firms, largely at their own instigation, and now they have ramifications which can best be represented in the form indicated below.

Fisons, Ltd., Harvest House, Ipswich.

This group incorporates the following subsidiaries, which do not manufacture superphosphate, and can be classed as compounders :—

Joseph Fison & Co., Ltd., Bramford.
 Packard & James Fison (Thetford) Ltd., Thetford.
 Packard & James Fison (Thetford) Ltd., Haddiscoe.
 Prentice Bros. Ltd., Stowmarket.
 Prentice Bros. Ltd., Gt. Yarmouth.
 Hart Bros. & Co. Ltd., Keadby.
 Quibell Bros. Ltd., Newark-on-Trent.
 Shepperson (Fertilizers) Co. Ltd., Kirton, Lincs.
 Langdale & Northern Fertilizers, Ltd., Newcastle.
 Renny, Forbes & Co. Ltd., Wembley.
 Geo. Hadfield & Co. Ltd., Liverpool.
 Spooner & Bailey, Ltd., Southampton.

The following firms in this group still continue to manufacture superphosphate :—

Doughty Goole Fertilizers, Ltd., Goole.
 Doughty Goole Fertilizers, Ltd., Lincoln.
 Anglo-Continental Guano Works, Ltd., Silvertown, E.16.
 De Pass Fertilizers, Ltd., Barking.
 J. & W. Maxwell, Ltd., Silloth.
 Blaydon Manure & Alkali Co. (1877) Ltd., Blaydon-on-Tyne.

Scottish firms in the group :—

J. G. Cunningham, Ltd., Burntisland.
 Thos. Ovens & Sons, Ltd., Bo'ness.
 H. G. McCreath & Sons, Berwick-on-Tweed.

National Fertilisers Group, controlled by Fisons, Ltd. :—

National Fertilizers, Ltd., Avonmouth.

The following firms are in this group :—

Corby Basic Slag, Ltd., Corby.
 Chas. Norrington & Co. Ltd., Plymouth.
 Burnard & Alger, Ltd., Plymouth.
 Gibbs Fertilizers, Ltd., Plymouth.
 Thos. Vickers & Sons, Ltd., Widnes.
 Basic & Phosphate Co., Newport.
 Vivians Fertilizers, Ltd., Truro.

* * * * *

The following firms are still working independently, and manufacturing superphosphate :—

West Norfolk Farmers' Manure & Chemical Co-op. Co. Ltd., King's Lynn.
 Lawes Chemical Manure Co. Ltd., Barking.
 Sheppy Glue & Chemical Works, Ltd., Queenborough.
 Crone & Taylor, Ltd., Sutton Oak, St. Helens.
 United Alkali Co. Ltd., Wigg Works, Runcorn.
 Edward Webb & Sons (Stourbridge) Ltd., Saltney, Nr. Chester.
 G. H. Anderton, Ltd., Howden, Yorks.
 Farmers' Co. Ltd., Barton-on-Humber.
 Lindsey & Kesteven Chemical Manure Co. Ltd., Saxilby.
 Chas. Middleton & Sons, Ltd., Worksop.
 Hy. Richardson & Co. Ltd., Skeldergate, Yorks.
 Eaglescliffe Chemical Co. Ltd., Eaglescliffe.

The following Companies do not manufacture superphosphate, but are independent of the groups :—

Cannock Agricultural Co. Ltd., Cannock.
 J. H. & A. Cole, St. Phillips, Bristol.
 Carr's Fertilizers, 181, Higher Lane, Lymm, Cheshire.
 Sulfurophosphate, Ltd., Devonport.
 Ormskirk Fertilizers Co., Burscough Bridge, Nr. Ormskirk.
 Abel Woodhead & Sons, Holmfirth.
 Henry Quennell, Fidlers Ferry, Warrington.
 Sulfuro Fertilizers, Ltd., Devonport.
 Currie, Rowlands & Co., Seacombe, Cheshire.
 John Austin & Sons, Allscott, Shropshire.
 Malton Farmers Manure & Trading Co., Malton, Yorks.
 Hy. Bell & Sons, Ltd., Hexham.
 Mays' Chemical Manure Co. Ltd., Bourne, Lincs.
 Alfred Nightingale & Sons, Ltd., Bedford.
 H. & T. Proctor, Ltd., Bristol.
 J. P. Harvey & Co. Ltd., Kidderminster.
 Cornish Fish Products, Ltd., King's Lynn.
 Pan Britannica Industries, Ltd., Waltham Abbey.
 Boots Drug Co. Ltd., Nottingham.
 Carters, Ltd., Raynes Park.
 Farmers' Manure Co. Ltd., Royston.
 Joseph Ashworth & Sons, Ltd., Frodsham Bridge, Warrington.
 Harrington Bone & Chemical Co., Macclesfield.
 John Peak & Co. Ltd., Bridgewater Chemical Works, Wigan.
 E. Smith & Sons, River Head, Louth, Lincs.

Western Counties Co-op. Asscn. Ltd., Bristol and Plymouth.

H. Burlington & Co. Ltd., Evesham.

F. Elgar & Son, Ltd., Faversham.

Messrs. Fisons, Ltd. must now be responsible for the production and sale of 500,000 tons of calcium superphosphate and about 150,000 tons of compound fertilisers per year, of which about 60,000 tons of the latter is now being marketed in the form of granular N.P.K. fertilisers. The foregoing tonnages represent more than half of the fertiliser business of Great Britain.

Messrs. Fisons, Ltd. have absorbed fertiliser works in strategic areas of Great Britain, and have been concerned largely in securing the commercial associations of such business, deciding later whether the manufacturing plant was of sufficient importance to warrant continuance of operations, or whether the particular regional area was capable of being supplied with fertilisers more advantageously from another of their adjoining works.

A firm of high reputation and no mean importance is the West Norfolk Farmers' Manure & Chemical Co-operative Co. Ltd. This is a co-operative farmers' undertaking, which appears to be conceived on sound lines, and to which, in our original book, we made the following reference:—

“. . . Indeed, there is much to be said for the co-operative system, as is exemplified by at least one important chemical manure company in East Anglia. Here is an enterprising company, having works which are favourably situated geographically, with modern plant, operating on a large scale, and administered on sound lines. A not inconsiderable portion of the capital of the company is held by farmers, who receive their supplies of fertilisers from the company. Thus there is a mutuality of interests, which it should be the endeavour of all intelligent and enterprising business men to foster.

“The peculiar needs of the farmer can with advantage be revealed under such an arrangement, and the trial of new compound manures or fertilisers under practical conditions can readily be arranged. Further, practical information concerning soil fertility is available, and this, along with scientific research and investigation, may result in the production of fertilisers which are specially adapted for the soil, and which are of marked economic value to the farmer.

“Moreover, in the disposal of the fertilisers, agents' commissions can be dispensed with, the products can be sold on favourable terms direct, and the farmer has the knowledge that he participates in any profits which accrue from the conduct of the operations of the fertiliser company. In other ways it is not improbable that a further consolidation of interests can be arranged. . . .”

The firm of importance in Scotland, in the superphosphate industry, is the Scottish Agricultural Industries Ltd., which is a subsidiary of the I.C.I., centred around J. & J. Cunningham, Ltd., of Leith.

Scottish Agricultural Industries Group under the control of Imperial Chemical Industries, Ltd. :—

The following firms in this group make superphosphate :

J. & J. Cunningham, Ltd., Leith.

Alex. Cross & Sons, Ltd., Glasgow.

John Miller & Co. (Aberdeen) Ltd., Aberdeen.

J. Milne & Co. Ltd., Dyce, Aberdeen.

Chas. Tennant & Co. Ltd., Carnoustie.

Daniel Wylie & Co. Ltd., Ayr.

The following five firms are also in this group, but do not make superphosphate :—

Aberdeen Commercial Co. Ltd., Aberdeen.

John Poynter, Sons & Macdonalds, Glasgow.

Ferguson, Ltd., Perth.

Gray & Taylor, Ltd., Perth.

J. & J. Wylie, Leith.

The following firm is independent of any group, and manufactures superphosphate:—

R. & J. Garroway, Glasgow.

Imperial Chemical Industries, Ltd., must not be overlooked in the foregoing connection. In the broad sense they are not manufacturers of calcium superphosphate (it is true that such a product is manufactured at Wigg Works, Runcorn, and by their subsidiary, Scottish Agricultural Industries, Ltd.). But their entry into the superphosphate industry is largely by way of the manufacture and sale of concentrated chemical fertilisers. These are manufactured essentially from phosphoric acid and synthetic ammonia, and such products as mono-ammonium and di-ammonium phosphates are produced. These can be incorporated in divers ways with potash, and N.P.K. chemical fertilisers in the form of granules are produced (*vide* page 6).

It is from this source that competition in an indirect manner proceeds at the present time. How far it will affect the development of the superphosphate industry, and the production by that industry of granulated compound fertilisers, cannot be said. To what extent such competition will develop depends largely on the reception given by the farmers and horticulturalists to concentrated fertilisers.

More need not be said about what may be called the personnel of the industry. The other aspect of importance is as to whether the industry is conceived on a sound economic basis. On this subject some appropriate observations were made in 1918 by the Departmental Committee on Sulphuric Acid and Fertiliser Trades. They remarked :

"This country possesses no natural advantages for the manufacture of superphosphates since both Pyrites and Phosphate rock have to be imported as raw materials. It is, therefore, natural that when the consumption of superphosphate in countries such as Spain and Portugal reaches a certain point, local manufacture is undertaken, and, with the advantage of proximity to the raw material, soon succeeds in overcoming the competition of imported superphosphate from less favourably situated countries.

"As in the case of sulphuric acid, the available plant was capable, if continuously worked, of producing considerably more than the actual requirements of superphosphate. The position with regard to manufacturing efficiency was somewhat varied. Most superphosphate works were associated with acid plants, and the larger producers were equipped with mechanical and labour-saving devices, which enabled them to produce as economically as the continental works. Some of the smaller works, however, and especially those which had suffered from the loss of the export trade, had not been kept up-to-date as the uncertain prospects of the trade led to unwillingness to incur outlay in development of plant.

"One advantage which the fertiliser trades enjoyed was the existence of active and energetic trade associations. Both the Sulphate of Ammonia Association and the Fertiliser Manufacturers' Association were able to render valuable assistance to the individual producers, especially by organised propaganda, with a view to the creation and expansion of markets for their products."

Unfortunately, the superphosphate industry of this country still depends almost wholly on rock phosphate imported from Algiers, Morocco, Tunis, and Egypt, with smaller quantities from the United States (such as Florida rock phosphate), and still smaller quantities from Russia (in the shape of Kola phosphate). Of late there appears to be an increasing tendency to purchase Nauru and Ocean Island phosphates. Something fundamental can be said about the importation of the two latter phosphates, in that they benefit Great Britain, Australia, and New Zealand. Apparently something of the order of 700,000 tons of these phosphates are shipped annually to Australia, 300,000 tons to New Zealand, and 100,000 tons to the United Kingdom and other countries. What has to be borne in mind in this connection is that the phosphate rock is sold at *cost price*, and obviously, the partner-countries benefit in this way.

The other raw material that concerns in an important way the superphosphate industry is the raw sulphur material from which sulphuric acid is manufactured. The total capacity of United Kingdom sulphuric acid plants, exclusive of H.M. factories, during the year ended June 30, 1938, was reported to be 1,948,000 tons of 70 per cent acid. During the year in question superphosphate manufacture absorbed 335,000 tons, and sulphate of ammonia 295,000 tons of 70 per cent acid. These figures represent 23.6 and 20.6 per cent respectively of the total sulphuric acid consumption, and indeed are the two major industries absorbing this mineral acid.

As regards the incidence of raw materials in the manufacture of sulphuric acid, the under-mentioned tables are of interest.

TABLE 53¹

Production of Sulphuric Acid and Consumption of Raw Material
(Tons)

Year	100 p.c. H ₂ SO ₄			Pyrites and others*	Spent oxide	Brimstone and H ₂ S	Zinc concentrates
	Chamber and contact	Chamber only	Contact only				
1935	936,300	689,300	247,000	371,400	156,500	50,900	126,500
1936	1,043,100	734,500	308,600	404,100	161,200	61,200	160,900
1937	1,100,000	757,400	342,600	405,200	165,100	82,000	158,800
1938	994,700	651,400	343,300	364,900	146,200	74,500	141,600
1939	1,119,600	705,200	414,400	406,900	156,600	92,900	161,100
1940	1,235,400	771,200	464,200	426,400	164,300	125,400	154,200
1941	1,167,300	714,800	452,500	356,200	151,100	139,800	143,800
1942	1,213,500	703,800	509,700	340,800	154,500	145,000	195,700
1943	1,201,200	681,500	519,700	311,300	193,100	136,100	191,900
1944	1,221,300	674,400	546,900	303,400	191,800	146,900	184,100
1945**	604,100	335,900	268,200	152,200	93,600	78,300	70,700

* These figures include not only pyrites, but also the tonnage of anhydrite now consumed in this country having been converted into the "equivalent" tonnage of pyrites.

** First six months.

¹ *Chem. Age*, 8th Dec., 1945, p. 539; and *Chem. Tr. J.*, 12th Jan., 1945, p. 56.

TABLE 54

Production of Sulphuric Acid and Consumption of Raw Materials
(In tons.)

Year.	100 per cent H ₂ SO ₄ .			Pyrites and others.†	Spent oxide.	Brimstone and H ₂ S.	Zinc concentrates.
	Chamber and contact.	Chamber only.	Contact only.				
1934	886,300	667,600	218,700	362,900	158,600	43,500	97,100
1935	936,300	689,300	247,000	371,400	156,500	50,900	126,500
1936	1,043,100	734,500	308,600	404,100	161,200	61,200	160,900
1937	1,100,000	757,400	342,600	405,200	165,100	82,000	158,800
1938*	514,100	343,000	171,100	187,300	69,400	37,400	75,600

* First six months.

† In "Pyrites and others" is included anhydrite

At the present time 20 million tons annually of coal is carbonised at the gasworks in Great Britain, and approximately 20 million tons per annum of coal is being treated at coke ovens, in the preparation of furnace and metallurgical cokes.

It is known that where the H_2S of the crude coal-gas is recovered by oxide of iron, by the dry purification method, an average of 12 lb. of sulphur is recovered per ton of coal carbonised. At the moment all the crude coke-oven gas is not freed from H_2S . It is, however, a distinct advantage to deprive such gas of hydrogen sulphide, for heat treatment of metals, and indeed, definite demands are being made for sulphur-freed coke-oven gas.

Ultimately, one can foresee that the gas and coking industries will produce something of the order of 12 lb. of sulphur per ton of coal carbonised, in the form of spent oxide containing say 50 per cent of sulphur on the wet basis. This would represent say 428,500 tons of spent oxide (50 per cent sulphur on the wet basis), annually, which is an appreciable advance on the quantities indicated in the above table.

It may be three or four years before this projected condition is reached, but everything points to its realisation.

Although the theoretical tonnage of 428,500 tons of spent oxide has not been reached during the war, it is known that the production of spent oxide has increased appreciably, and probably not much less than 250,000 tons per annum has been reached. Spent oxide assumed such importance during the war that since May, 1941 it has been privately controlled. Although gas undertakings

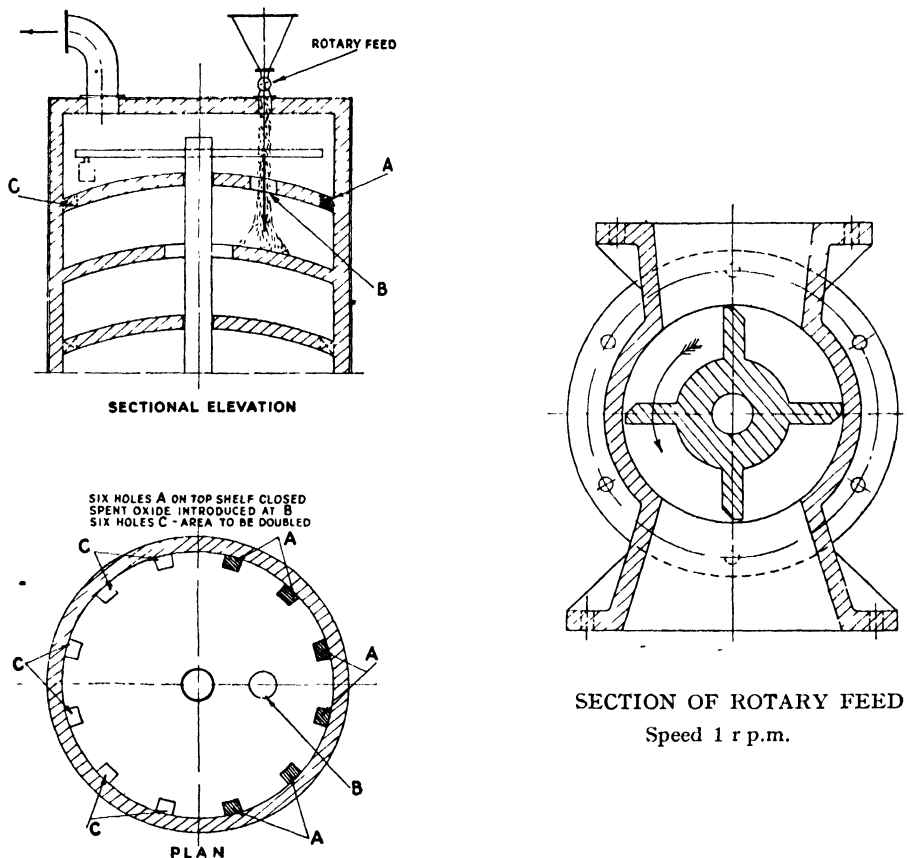


Fig. 149 —DIAGRAMMATIC SKETCH OF MECHANICAL PYRITES BURNER, SHOWING ADAPTATIONS NECESSARY FOR SPENT OXIDE COMBUSTION.

have not been given a pro-rata price per unit of sulphur, as contrasted with brimstone or pyrites, they have certainly received a consideration in the matter of price, but not one which can be regarded as at all adequate in the circumstances. Sulphuric acid works hitherto using pyrites have been switched to spent oxide, and mechanical burners have been modified, as is indicated below, and as is shown in Fig. 149.

The rate of combustion of spent oxide is appreciably greater than that of pyrites, and to avoid local overheating adjacent to the rotary feed it is desirable to by-pass the first shelf, and deposit the spent oxide on the second, near the outlet of the third shelf. Similarly, as a further precaution the passage of the burner gases is diverted from the falling material towards the outlet of the burner, six ports on one semi-circular portion of the top shelf being closed, and the remaining six ports being doubled in area. It has also been necessary to admit the bulk of the air for combustion to the shelf on which the spent oxide is fed. Fig. 149 shows these adaptations diagrammatically, and indicates the type of rotary feed which has been found, in practice, to be most suitable for ensuring a uniform supply of spent oxide without hitch. The feature of the arrangement is that the arms of the rotary feed have only a knife-edge contact with the housing, thus reducing the possibility of jamming.

The Chief Alkali Inspector is still pursuing his examination of most of the spoilbanks at the collieries throughout the country. The spontaneous combustion of these spoilbanks is attributed to an accumulation of heat generated by the slow oxidation of carbonaceous matter, and possibly pyrites. Where air cannot gain access, there is no possibility of spontaneous combustion, but in the majority of cases it is true to say that air does come in active contact with these spoilbanks, and local nuisance is caused. In some cases colliery companies have deputed chemists to investigate the problem.

The Chief Alkali Inspector has suggested that the work could with advantage be undertaken on a co-operative basis, and he has expressed gratification at the fact that the Yorkshire Advisory Committee on Mining Research proposes (*a*) to inquire into methods by which the extinction of these colliery spoilheap fires can be effected, and (*b*) to seek methods by which they can be avoided. It is understood that a programme of work is in preparation, and that the investigation is to be pursued with diligence.

The material which is most liable to spontaneous ignition is inferior (banded) bituminous coal and this liability is increased by the presence of pyritic material. It is known that in the Northumberland colliery districts greater attention is being given to the picking of the coal brasses from the belts, and it is not improbable that coal brasses containing from 44 to 50 per cent of sulphur will shortly be available for disposal.

One of the authors has dealt with the combustion of coal brasses in some detail.¹ Why this subject is mentioned here is because the recovery of coal brasses, as such, would represent a distinct economy, compared with their carbonisation with the better coals. It is costly to have to remove hydrogen sulphide from crude coal-gas, even with oxide of iron, by the dry purification method. An examination (1938) of gas companies' accounts will make this clear. No gas undertaking derives a profit from its dry purification: in point of fact, it represents a debit of the order of 0.315d. per thousand cubic feet, which, based on a yield of 14,000 cubic feet per ton of coal carbonised, represents a cost of say 4.4d. per ton of coal, or about £3 8s. 6d. per ton of sulphur.

About 30,000 tons of coal pyrites in 1945 were being used in the manufacture of sulphuric acid. The Ministry of Supply (Sulphuric Acid Control) install and operate the processes, and sell alike the pyrites and the separated coal. Three processes of treatment have been developed: one relates to crushing, screening and cleaning the coal waste, which presumably involves the use of Wilfley tables: in the second air separation is the governing principle: the third is an elutriation method, representing an adaptation of the applied principles of the Baum washer. It has been found that the economic optimum content of sulphur in coal pyrites is 44-45 per cent. Generally speaking, the particle size of coal pyrites is less than that of Spanish pyrites, and as the rate of combustion is greater the finer the particle size, in order to avoid inconvenience due to excessive temperature in the top shelves of the mechanical burners employed, it is customary to mix a predetermined percentage of Spanish pyrites, to arrest a too-rapid combustion.

¹ *Gas Journal*, Feb. 5th, 1918, p. 246.

But despite this, there can be no doubt that if the superphosphate industry had allied itself to the gas and coking industries, not only would it have had a sound foundation in the matter of the sulphur material that it needs, but equally, it would have been able to establish itself firmly in the matter of ammonia. With care, something of the order of 6 lb. of ammonia per ton of coal carbonised can be recovered, and basing on the carbonisation of 40 million tons of coal per annum, this would represent the equivalent of say 857,000 tons of sulphate of ammonia, 25 per cent NH_3 . Much of this ammonia could advantageously have been produced in the form of concentrated gas liquor, and could have been treated economically at superphosphate works, either in the production of sulphate of ammonia, or ammoniated superphosphate. As it is, the superphosphate industry now depends on varying qualities of sulphur material, such as pyrites, spent oxide, and zinc blende.

In the view of the authors, there is still need for a reconsideration of this matter. By suitable modification of pyrites mechanical furnaces, these could be adapted to the combustion of spent oxide, and the electrostatic precipitators which are almost invariably attached to them could be operated without hitch.

Where suitable furnaces do not exist, one would suggest the installation of the Harris mechanical furnace, because of the inherent advantages which this equipment possesses.

The combustion of sulphur-containing materials, in hand and mechanical burners, was the subject of a paper by one of the authors in April, 1925.¹ This contribution has been acclaimed as one of the most comprehensive of its kind. Yet if space permitted, a wealth of additional information could now be afforded.

In the contribution in question attention was directed to the fact that there was a decline in the use of pyrites in the United Kingdom as between 1913 and 1923-24. The figures are still of interest, and are given below :

TABLE 55

Sulphur-containing Material used in the United Kingdom

	1913. Tons.	1923-24. Tons.
Pyrites	810,000	350,000
Spent oxide	110,000	148,000
Sulphur	3,000	66,000

Is the decline in the use of pyrites—a decline which still continues—attributable to price considerations, or have the sulphuric acid manufacturers of this country preferred to take the easier course, and use material which gives very little trouble in combustion, and involves little labour and supervision? The latter factors in a measure doubtless account for what has occurred. Spanish and Portuguese pyrites are for the most part arsenical, and obviously, if arsenic-free sulphuric acid is in demand, one must resort to the process of de-arsenication, which is a troublesome one, on account of the bulky nature of the arsenic sulphide precipitate, and the difficulty which arises in its disposal.

Moreover, in the process of de-arsenication dilution of the sulphuric acid occurs, and concentration of such diluted acid is necessary. All these operations involve additional expenditure, which many acid manufacturers seem inclined to avoid. Perhaps on balance, taking overall efficiency into account, in relation to price considerations, as between sulphur and pyrites, there is something to recommend the employment of sulphur, in the view of many acid manufacturers. Yet it is felt that the monetary advantage would generally favour the use of pyrites.

It will be found, however, that at most superphosphate factories in Great Britain pyrites or spent oxide is the raw sulphur material employed. This is largely because arsenic-free sulphuric acid has never been called for in the manufacture of calcium superphosphate.

¹ Proceedings of the Chemical Engineering Group, Vols. VIb and VII, pp. 111-129.

Elsewhere in this book it has been urged that the trace elements, such as iron, sulphur, copper, manganese, boron, and zinc, many of which are contained in the dust from the combustion of pyrites fines or concentrates, and some, indeed, from the combustion of spent oxide, have a definite value, when associated with the calcium superphosphate. It is for this reason that it is unwise to pursue electrostatic precipitation of the burner gases resulting from the combustion of pyrites or spent oxide too efficiently. It is equally for this reason that the contact process may not necessarily be the best for the production of sulphuric acid which is to be used for the manufacture of calcium superphosphate or ammonium sulphate.

One of the authors has been responsible for the erection of plant for the manufacture of sulphate of ammonia, in which arsenical sulphuric acid and concentrated gas liquor are used, the ferrous iron content of the sulphuric acid being an important factor, by forming a nuclear alum—a ferrous ammonium sulphate—in the production of sulphate of ammonia crystals of hard quality, having a length-to-breadth ratio of 3 : 1, and attractive grist characteristics.

A recent development in the matter of sulphur material may appropriately be referred to here. This relates to the increasing use of flotation pyrites, which was a novelty a few years ago, and indeed is something of an innovation where a conservative policy still obtains. The flotation pyrites of the Cyprus Mines Corporation has the following grist characteristics :

Remaining on 18 B.S.S.	.	.	1.5 per cent.
" 30 "	.	.	0.7 "
" 60 "	.	.	10.3 "
" 85 "	.	.	16.2 "
" 100 "	.	.	13.2 "
" 120 "	.	.	14.0 "
" 200 "	.	.	26.2 "
Passing 200 "	.	.	17.9 "

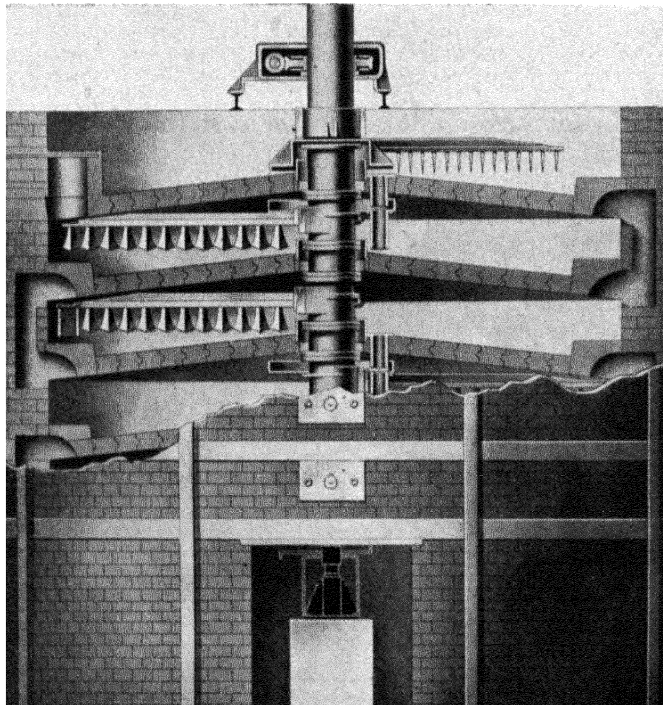


Fig. 150.—HARRIS MECHANICAL FURNACE WITH FOUR WORKING HEARTHES : PART ELEVATION, PART SECTION

But we are assured that where roasting practice is efficient, the sulphur content of the resulting cinders ranges between 0.5 and 1.0 per cent. One would conclude that the combustion in mechanical furnaces of such flotation pyrites would lead to the formation of much dust in the burner gases, and that the cost of electrostatic precipitation would be heavy. This, apparently, is not the case. There is something unusual in the physical character of the flotation cinders arising in the combustion of Cyprus Mines Corporation flotation pyrites. The cinder particles are of greater density, and do not appear to be entrained to the same extent as dusts arising in the combustion of other qualities of pyrites.

It is desired to revert here to the combustion of spent oxide in mechanical furnaces, because it is felt that the calcium superphosphate industry must attach itself to this raw material sooner or later.

There are several excellent mechanical burners suitable for the combustion of spent oxide, of which the Harris, Herreshoff, Wedge, and Wyld may be mentioned. The Herreshoff and Wedge furnaces demand the installation of electrostatic precipitators, if reasonably dust-free burner gases are to be obtained. The flue for the travel of the burner gases can be arranged in connection with the Wyld mechanical spent oxide burner in such a way as largely to obviate the entrainment of dust.

The Harris mechanical furnace appears to provide the best solution of the dust problem, and yet yields sulphuric acid possessing satisfactory qualities for calcium superphosphate and sulphate of ammonia manufacture. The latest form embodies several new features, which can be summarised thus :

(1) The use, on each hearth, of a dust-preventing device, which completely isolates the falling spent oxide from hearth to hearth, from the passage of the burner gases. The correct working of these devices is controlled, when necessary, from inspection doors situated in the walls of the furnace.

(2) The employment of cast steel, instead of cast iron, for the central shaft, which is constituted of small units, or elements, which are easy to replace, if ever necessary.

(3) The use of a special heat and corrosion-resisting steel alloy for the arms, removable rakes, and dust-preventing devices.

The effect of the foregoing provisions has been to suppress dust, and to effect a reduction in repairs and maintenance expenditure. As regards the separation of dust, the authors know, from what has been elicited independently, that the Glover tower acid (148° Tw., 80 per cent) contains about 0.04 per cent of iron, and the chamber acid a correspondingly lesser content. Further, the cost of a 10-ton furnace in 1939 was of the order of £2,250, and it will be appreciated that no electrostatic dust precipitator is called for : that the brickwork of the top shelves is guaranteed to serve for seven years : that the bottom brickwork only necessitates renewal about every twelve years.

Since the adoption of the new type of arms, in nickel-chrome-tungsten steel, it has been possible to dispense with air- or water-cooling. Air is used now only for the central shaft, and the quantity required in connection with a 10-ton furnace is approximately 1,000 cubic feet per minute.

The usual sizes of Harris furnaces are :

- (1) 7 to 8 tons daily roasting capacity.
- (2) 9 to 10 " " " "
- (3) 15 " " " "
- (4) 20 to 25 " " " "

Furnaces can always be adapted to suit local requirements. The characteristics in relation to capacity are given below :

	Capacity. Tons per day.	Number of working hearths.	Approximate height of furnace.	Outside diameter.
			ft. ins.	ft. ins.
1	7-8	4	15 0	15 10
2	9-10	5	17 0	15 10
3	15	6	19 0	17 6
4	20-25	8	23 0	19 0

Typical Harris furnaces, one circular and the other rectangular, are shown in Figs. 150 and 151.

The 7 to 8-ton furnace is provided with four working hearths, the roof of the top hearth serving as a drying, or desiccating floor. The spent oxide, after being crushed and screened to pass $\frac{1}{4}$ -in. mesh, is fed to the drying hearth by means of a feed table and elevator, which admits of a uniform supply. At this point spent oxide is partially dried on this open hearth. The drying hearth



FIG. 151.—VIEW OF TWO HARRIS CIRCULAR SPENT OXIDE FURNACES

is equipped with arms and rables, which conduct the spent oxide to the centre, where it is automatically fed into the furnace through a dust-preventing device, provided in special alloy. The central shaft, which is air-cooled, is constituted of double-flanged cast steel elements, which allow of easy changing, if ever necessary. The central shaft is mounted on a double ball-bearing screw jack, which is adjustable for height. The arms are of the special steel alloy already referred to, air-cooled, and are practically indestructible under the temperatures and conditions to which they are subjected. The burner gases have practically no effect on the arms, which is in marked contrast to what occurs when cast iron or cast steel arms are used. Equally, very little corrosion arises to the removable rables or rakes, which only suffer in the hotter zones.

The products of combustion pass completely over each hearth of the furnace from top to bottom. The gas uptakes from each hearth are arranged on opposite sides of the furnace, as shown in Fig. 152. These uptakes are made of special fireclay blocks, arranged partly in the furnace wall, and partly in the arches, and rarely occasion any cleaning. The arms pass under the openings, as is shown in Fig. 153, and thus obviate any blockage of the uptakes. Specially designed drop boxes and seals (see Fig. 153) for conveying the spent oxide from hearth to hearth are situated on the centre and

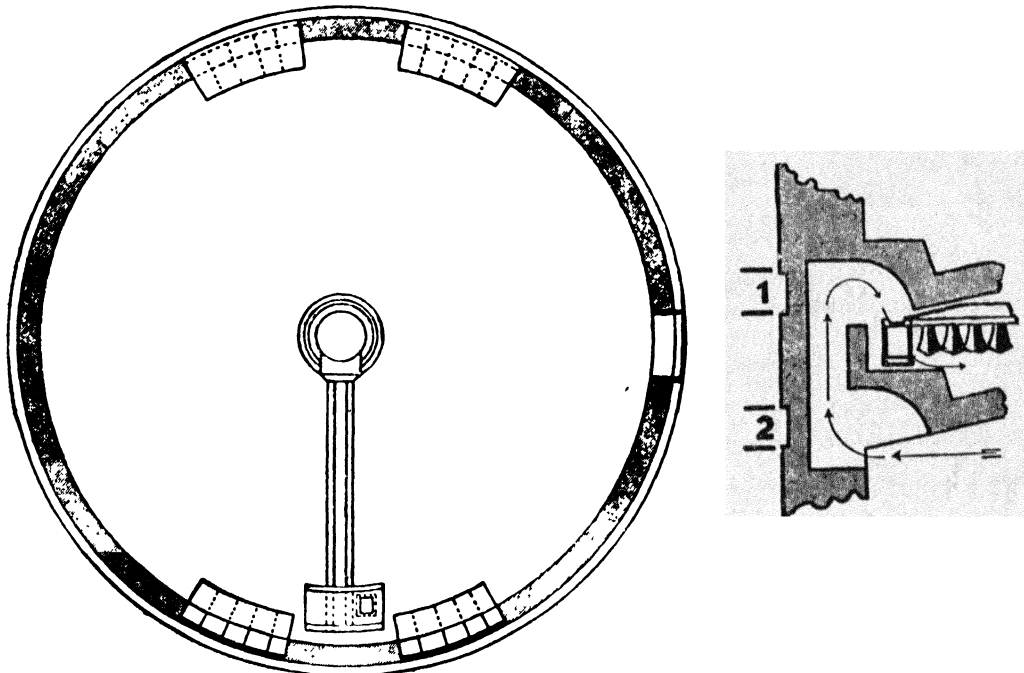


FIG. 152.—SECTIONAL PLAN AND ENLARGED SECTIONAL ELEVATION OF "HARRIS" SPENT OXIDE BURNER, SHOWING GAS UPTAKES ON OPPOSITE SIDES OF FURNACE, ARM WITH DUST-PREVENTING DEVICE, AND ARROW LINES INDICATING TRAVEL OF GAS FROM HEARTH TO HEARTH

periphery of alternate hearths, and admit of the descent of the oxide to the hearth below, without creating any dust, and moreover shield the falling material undergoing combustion, from the passage of the gases. It should be emphasised in the latter connection that in most mechanical furnaces, entrainment of dust is promoted by the failure of the equipment to separate the descending material undergoing combustion from contact with the ascending burner gases.

The combustion efficiency in connection with the Harris mechanical furnace is such that the residue, or ash, from the burning of spent oxide, does not contain more than 0.05 per cent of sulphur soluble in CS_2 , and as the latter is the test on which the sulphur content of spent oxide is purchased, the following results obviously apply.

8 cwt. of residue per ton of spent oxide=

$$0.4 \text{ ton} \times 0.05 \text{ per cent sulphur} = 0.02 \text{ per cent sulphur.}$$

Percentage of sulphur in original material :

$$50 : 100 :: 0.2 \text{ per cent loss} : X \\ x = 0.04 \text{ per cent sulphur loss}$$

Combustion efficiency, 99.96 per cent.

Of course, the determination of the combustion efficiency is not quite so easy as is represented above. One of the authors has pointed out that "there can be no doubt that the combustion efficiency of mechanical furnaces is higher than in hand burners, but no comparison can be made unless the same materials are burned in the respective burners, and the method of determining the percentage loss of sulphur is undertaken in the way indicated below.

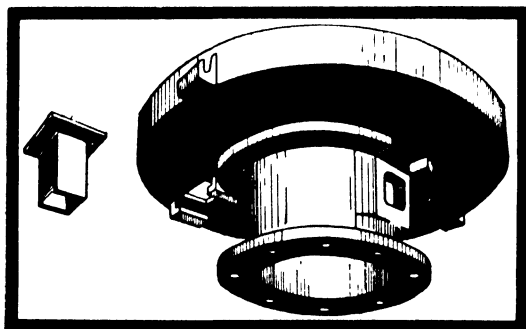


FIG. 153.—PORTION OF CENTRAL SHAFT, SHOWING THE DUST-PREVENTING SEAL AND DROP BOX

“Determination of the sulphur content by extraction with carbon bisulphide is misleading. The combustion method could be adopted, but for the fact that the original spent oxide contains sulphur compounds, some of which are acid-yielding, while others are not.

“Thus, to arrive at an accurate combustion efficiency, the free sulphur, total iron as Fe₂O₃, and sulphur compounds other than free sulphur, must be determined in the original spent oxide and in the burnt residue. A determination has been made of spent oxide which was subjected to combustion in a Herreshoff mechanical furnace. The results are subjoined :

TABLE 56

	Spent oxide.		Burnt residue.	
	Actual percentage.	Fe ₂ O ₃ = 100.	Actual percentage.	Fe ₂ O ₃ = 100.
Free sulphur	51.25	359.10(A)	0.04	0.074(C)
Total iron as Fe ₂ O ₃	14.27	—	54.25	—
Sulphur compounds other than sulphur	1.04	7.34(B)	5.13	9.47(D)

The loss of free sulphur is arrived at from the above results by the following formula :

$$100 \times \frac{C + D - B}{A}$$

$$= \frac{0.074 + 9.47 - 7.34}{359.10}$$

$$= 0.61 \text{ per cent sulphur.}''$$

The foregoing only represents an isolated test, and must not, therefore, be regarded as an average figure. When spent oxide is undergoing combustion the major portion of the air is introduced in the top and second shelves, and the residue is discharged, relatively cool, from the bottom shelf.

The burnt residue arising from the combustion of spent oxide at one large works in the Midlands, using Harris mechanical furnaces, is loaded direct into trucks and sent to the blast furnace, where, apparently, it causes little difficulty, and where the iron is recovered in the form of pig iron.

We have pursued the aspect of sulphur material, and particularly spent oxide and its combustion, at some length, because it is here that we perceive ground for a justifiable foundation for the British calcium superphosphate industry in an indigenously produced material. This justification was lacking when the matter called for serious inquiry in 1918 by the Departmental Committee on Sulphuric Acid and Fertiliser Trades.

Design and Conduct of a Calcium Superphosphate Works

The manufacture and sale of calcium superphosphate should not constitute the only activity of a fertiliser business, otherwise its profitable conduct is doubtful, however expert may be the

works staff in the economic handling of the raw materials and finished product. It is a *sine qua non* that compound fertilisers (preferably granulated), should be manufactured, and that there should be a live selling organisation for such products, working in close conjunction with the chemical department. It should be decided at the outset, as a policy, whether the fertiliser company is to act as bankers to the clients, or whether the sales are to be effected through agents, who would be expected to pay cash on the 20th of the month following delivery.

No one who has examined the accounts of a fertiliser company manufacturing calcium superphosphate can fail to be impressed with the fact that with many transactions, twelve months' or two years' credit has to be given to many clients. This system of deferred payment (congealed capital, which in large constructional contracts calls for instalment payment at agreed stages, and at times an initial instalment) must be contemplated in the selling price of the fertiliser products, otherwise the conduct of the company will be uneconomic.

The fact has to be conceded that the farming industry as a whole was a partially distressed industry in 1939. The second world war has changed materially the lot of the farmer. Markets for his products are now guaranteed, and certain subsidies have been arranged, which give him a security he never hitherto possessed.

Capital expenditure on buildings and plant is a vital consideration. Efficient and economic production must be secured, with a minimum expenditure of capital. As between one type of plant and another, the items that call for evaluation as regards annual costs are :

- (1) Interest on first cost.
- (2) Depreciation and obsolescence.
- (3) Cost of operation.
- (4) Cost of supplies, and
- (5) Cost of attendance and repairs.

The selection of a site in relation to demand is equally one calling for the exercise of clear thinking. The larger the production unit, other things being equal, the cheaper will be the cost of production. But if the product of a large production unit is to be distributed over long distances, and the costs of transport by sea, canal, or river are greater than the economy of production, obviously, a mistake has been made in the size of the unit.

Selecting the Site.—What are the considerations governing the selection of the site of a fertiliser works? Such site should be as centrally disposed in the area of demand as possible : it should have sea, or river, or canal facilities : it should be land capable of carrying 15 cwt. to 1 ton per square foot, thus avoiding the necessity for piling and the construction of concrete rafts. It should have satisfactory rail and road facilities : its cost should be reasonable, and the rates of the rural, urban district, town or city council should be relatively low. Importance is attached to the reception of the phosphate rock and pyrites or spent oxide in ships direct from the port of origin. Transshipment to barges or railway wagons should be obviated, if at all possible. Dependent on the magnitude of the demand for a given area, an economic unit of plant in this country is one capable of producing fifty to sixty thousand tons of calcium superphosphate per annum. The cost of such a plant depends on a number of considerations, to some of which reference has already been made. The cost of the calcium superphosphate production unit is a relatively minor item, compared with the cost of the sulphuric acid plant, the grinding and screening-bagging units, the granulation plant and the mechanical means to be afforded for the economic handling of the raw materials which go to constitute the compound fertilisers and the finished fertiliser products.

A batch den having a capacity of 25 tons, and capable of producing, based on three-hour cycles, 75 tons of calcium superphosphate in nine hours, would cost approximately £2,000. A Broadfield continuous den, capable of producing 10 tons per hour, which, operating for 20 hours per day (allowing adequate time for cleaning purposes) produces 200 tons per day of 24 hours, would cost about £4,000. An Oberphos plant is certainly a much more expensive one, both as regards initial capital outlay and operating costs. It is certain, therefore, that the calcium superphosphate-producing plant *per se* is not a cardinal consideration. Capital expenditure alone is not

the desideratum. Operating costs (a constant charge), costs of repairs, and maintenance and obsolescence, as already remarked, are in many cases the vital factors.

It is important to construct serviceable buildings for the storage of the phosphate rock and the

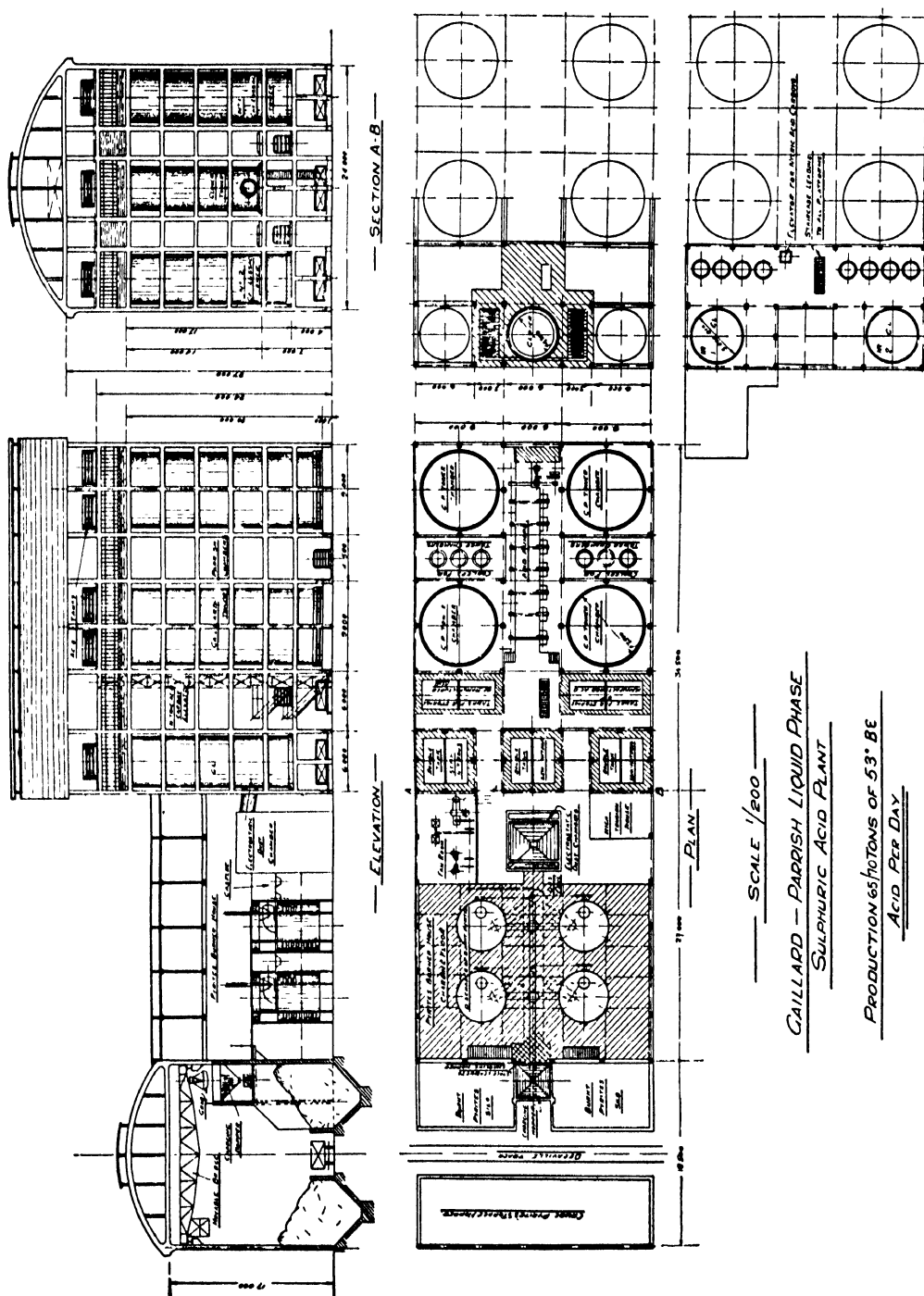


FIG. 154.

calcium superphosphate, and for housing the calcium superphosphate manufacturing unit, *at a minimum of cost.*

The advantage of an efficient and economic unit of sulphuric acid plant cannot be over-estimated. Some features of one of the modern types of plant will be briefly indicated. Other sulphuric acid plants that should be considered are the Mills-Packard water-cooled type, and the Moritz.

Fig. 154 shows the layout of a Gaillard-Parrish sulphuric acid plant, designed essentially to facilitate the economic handling of the pyrites and pyrites cinders. The ferroconcrete silos, and the provision of an overhead single girder travelling electric crane, which runs out to the wharf and enables the pyrites to be grabbed from the hold of the ship, and similarly enables the pyrites cinders to be tipped into the hold, all contribute to this end.

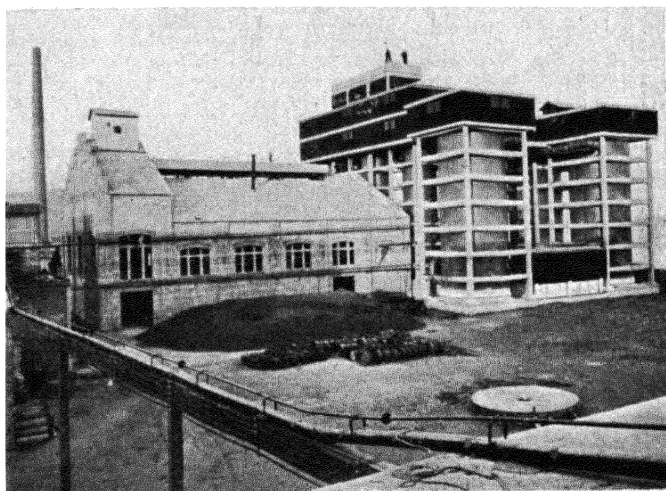


FIG. 155.—VIEW OF A GAILLARD-PARRISH SULPHURIC ACID PLANT: BUILDING AND FRAMEWORK CONSTRUCTED OF FERROCONCRETE

The mechanical burners for pyrites are of a robust type, calculated to operate without undue breakage of rabblies or arms, especially if the special alloy steel now available (such as high-chromium steel, "ERA.H.R.4₁" for the teeth, and nickel-chrome-tungsten steel "E.R.A.C.R.2₁" for arms, are employed, and the electrostatic precipitator admits of controlled elimination of the dust entrained in the burner gases, and allows of the production of a clean Glover acid under efficient conditions.

Fig. 155 is a photograph of a unit of a Gaillard-Parrish sulphuric acid plant, the skeleton frame-work and buildings of which are constructed of ferroconcrete. Not only is this a cheap form of material, but it possesses stability, non-corrosive properties, and withal has the advantage of being fireproof.

Such a unit of plant presents an attractive appearance, and has utilitarian merits. Where the liquid phase system is adopted, without entering into a detailed description it can be said that it admits of sulphuric acid being manufactured under the most economical conditions. Not only is the exothermic heat of reaction removed, in an inexpensive and rational way, but the bombardment of the gaseous reactants by liquid sulphuric acid in an extremely fine state of division accelerates the production in an amazing way, and reduces the space-time factor to something of the order of $2\frac{1}{2}$ to 3 cubic feet per lb. of sulphur per 24 hours.

It should be remarked here that the skeleton framework for the erection of the lead constituting the Gaillard-Parrish chambers can be either of ferroconcrete, as is shown in Fig. 152, or of steel, or of pitch pine. Moreover, the tower chambers can be either cylindrical, or hexagonal, as is shown in Fig. 153, or they can be octagonal or square. The hexagonal, octagonal, and square types of Gaillard-Parrish tower chambers entail a lower cost for the erection of the leadwork than the cylindrical ones, and from this point of view are commendable. From the viewpoint of the dispersion of sulphuric acid it matters little whether the tower chambers are circular, hexagonal, octagonal, or square.

Turbo dispersers of two sizes are available, one for the dispersion of 900 gallons per hour, the other for the dispersion of 1,600—1,800 gallons per hour. These turbo dispersers are of the disc type, for lateral dispersion, or of the conical type, for central dispersion. Fig. 154 represents the latest and most approved type, which has given satisfaction wherever it has been installed, and is of the conical type.

The advantage of acid dispersion lies in the fact that the whole of the leadwork of the vertical walls can be irrigated with cooled acid which, it has been found in practice, is protective against the attack of the lead. Apart from the cooling due to the irrigation in question, the whole chamber is filled with a fine mist of acid vesicles, which bombard the reactants and accelerate sulphuric acid production. It is much easier to cool a stream of acid in a concentric cooler than it is to ensure cooling by water irrigation on the outside of a tower chamber.

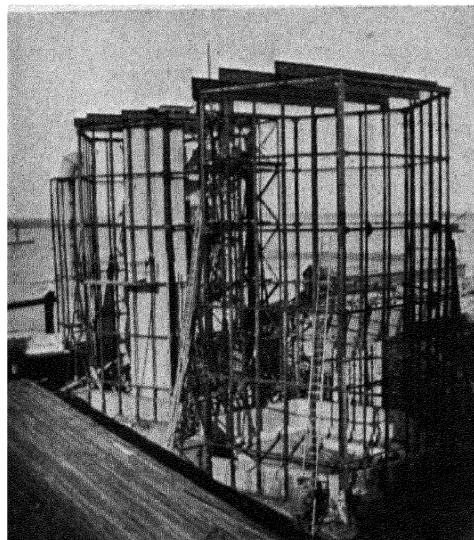


FIG. 156.

PARRISH HEXAGONAL TOWER CHAMBERS
IN COURSE OF ERECTION

resisting tiles, used in conjunction with acid-resisting cement, as the materials of construction of a nitrous chamber."

On the subject of the protective influence of cooled acid irrigation, the following weighings of sample cuts of chemical sheet lead, taken from a set of sulphuric acid plant (Gaillard-Parrish liquid phase type), after fourteen years' continuous operation, are illuminating. The chambers in question were originally built of 8 lb. per sq. ft. chemical sheet lead, containing 0.07 per cent of copper. It will be observed that the loss in weight of lead in the first two chambers is relatively small. No. 3 chamber is a partially nitrous chamber, and greater corrosive effect would naturally be anticipated. No. 4 chamber is the nitrous chamber, and one can understand the diminution of weight here.

One of the authors has affirmed on several occasions that "there is much to recommend the consideration of a chamber constituted of acid-

TABLE 57

Chamber.	Position.	Weight per sq. ft. (Taken on opposite axes).			
		lb.	oz.	lb.	oz.
1	Bottom	7	8	7	12
	Centre	8	-	8	-
	Top	7	8	8	-
2	Bottom	8	-	8	-
	Centre	7	-	7	8
	Top	7	12	8	-
3	Bottom	6	12	7	-
	Centre	7	4	7	4
	Top	8	-	7	4
4	Bottom	3	4	4	-
	Centre	3	4	3	12
	Top	3	-	5	8

From a very careful examination of the samples of lead drawn from the chambers in question, the following conclusions have been reached :

- (a) That it is desirable to incorporate between 0.065 per cent and 0.07 per cent of copper in chemical sheet lead for sulphuric acid chambers.

- (b) Microscopic examination in which a certain amount of grain boundary movement is seen, suggests that vibration should be reduced to a minimum, and sudden temperature changes avoided. The latter is achieved in the Gaillard-Parrish liquid phase system, but it is desirable, if increased length of life is to be given to tower chambers, to enclose these in a building, rather than to erect the exposed type of tower chamber.
- (c) There is no doubt that the Gaillard-Parrish liquid phase system of sulphuric acid manufacture prevents rapid corrosion of the chemical sheet lead, by affording a protective film of acid.

No modern sulphuric acid plant should be without an ammonia oxidation plant, for the production of the oxides of nitrogen required as a catalytic medium for the conversion of the SO_2 to SO_3 in the manufacture of sulphuric acid. It is a simple matter to distil liquor ammonia containing 20–25 per cent NH_3 , and to introduce air in suitable proportion, so that following dephlegmation (i.e. the removal of the steam from the steam-ammonia-air mixture, leaving the distillation unit) the ammonia-air mixture has a ratio of 1 : 9 by volume.

If the converter containing the platinum-rhodium or platinum gauze is placed adjacent to the first chamber of a set, there should be no difficulty in obtaining suitable conversion of the ammonia to oxides of nitrogen without hitch, and in an almost automatic manner. Placing the converter at this point, and ensuring that the gaseous oxides of nitrogen, along with any liquid nitric acid, are introduced into the chamber without the possibility of contact with its chemical lead walls, one need not resort to serpentine condensers, which invariably bring in their wake troubles from broken pipes and leaky joints.

Using a platinum-rhodium gauze under the foregoing conditions, it should convert 30,000 to 40,000 lb. of ammonia before it becomes inactive. Even then, its salvage value represents about 60 per cent of the original cost of the gauze. The cost of converting ammonia, at an efficiency of 90 per cent, to oxides of nitrogen, basing on a consumption of nitrate of soda on sulphur of 3 per cent, will be of the order of 7½d. per ton of 70 per cent acid, assuming the cost of the liquor ammonia, 25 per cent NH_3 , to be £5 per ton. The cost of the platinum-rhodium gauze, steam for distillation, and other incidental items, will not represent more than 2d. per ton of 70 per cent acid.

This is a distinct advance in technique, and, not less so, a definite economy. It is an aspect that may call for more elaborate treatment at a later stage.

Fig. 158 shows five distillation units, operating in conjunction with five converters, and constitutes the ammonia oxidation plant at a large sulphuric acid works.

Fig. 159 shows the rotameters (the device for measuring the rate of feed of the liquor ammonia), air flow and back-pressure gauges, all of which are valuable adjuncts to the efficient control of the operation of ammonia oxidation units.

Only one further word need be added on this aspect. Where a sulphuric acid unit has to work intensively, there should be appreciable flexibility of the ammonia oxidation unit, or otherwise a small nitric acid plant should be erected, capable of operating in automatic way, without labour, and without involving much supervision. One of the authors has evolved such a plant, which can work with an impure form of ammonia (available at much less cost than liquor ammonia of 25 per cent NH_3) producing nitric acid of 50–55 per cent HNO_3 at a remarkably low cost. Nitric acid is a valuable raw material for any sulphuric acid unit, as its response, when applied to the Glover tower is immediate.

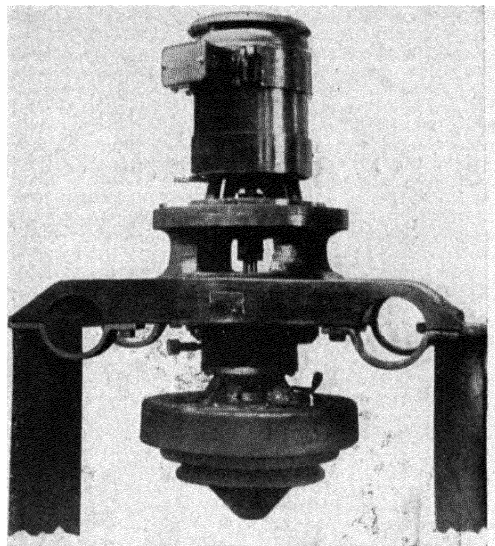


FIG. 157.—PARRISH IMPROVED TYPE OF TURBO DISPERSER

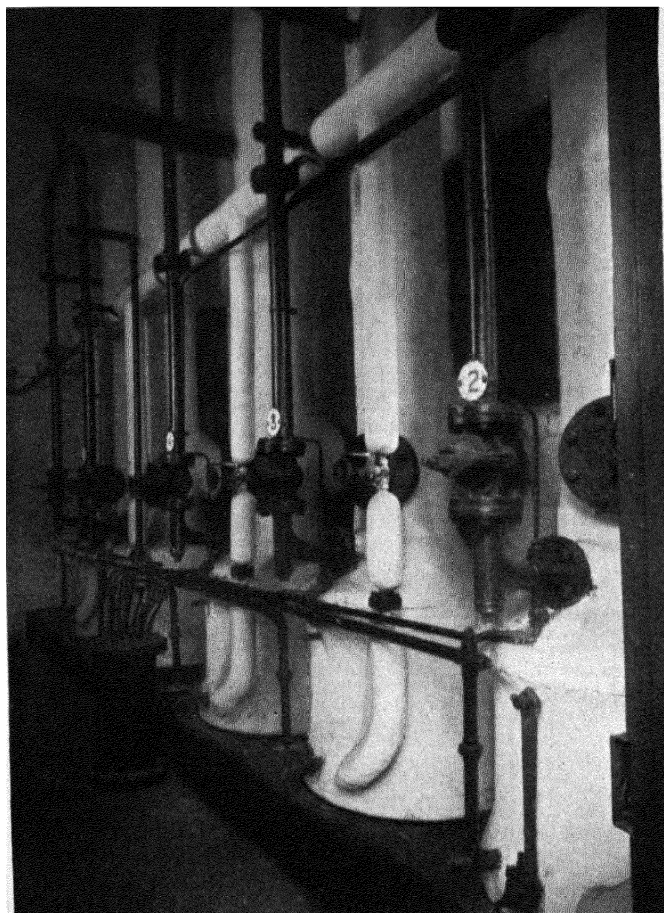


FIG. 158. DISTILLATION UNITS FOR LIQUOR AMMONIA
--AMMONIA OXIDATION PLANT (PARRISH TYPE)

Chemical sheet lead has advanced in price from £25 per ton in 1939 to £38 per ton in May 1945. To-day the capital value of a contact sulphuric acid plant cannot be regarded as much less than £7 10s. per ton of annual capacity of 100 per cent acid. This is for a contact plant, including buildings and normal foundations, but, of course, does not include the provision of railway sidings, roads, offices, lobbies, workshops, etc., etc. The capital cost of a chamber sulphuric acid plant to-day on the foregoing basis, in terms of 100 per cent H_2SO_4 , cannot be much less than £6 10s. per ton. Thus, a fertiliser works for the production of the equivalent of 50,000 tons of calcium superphosphate, 35 per cent $Ca_3P_2O_8$, will cost about £225,000. This sum should cover the provision of wharf and railway facilities, and working capital based on 12s. per ton of calcium superphosphate manufactured annually.

In the view of the authors, there is no need for elaborate manufacturing plant. The simpler it is, provided it produces a satisfactory final fertiliser, the better. Given efficient and economic production, adept and economic handling of materials is the primary consideration.

Simultaneous Production of Sulphuric and Nitric Acid.—The simultaneous production of sulphuric

and nitric acid has been the subject of much consideration, and plant development, during the last five or six years. Such a process (Kachkaroff-M.-P.) has two outstanding features. By passing large quantities of oxides of nitrogen in excess of what is required for the manufacture of sulphuric acid through the tower chambers, the space-time factor is reduced appreciably, and the production of sulphuric acid per unit volume reaches phenomenal figures.

Moreover, the "nitroses" formed by the absorption of the regenerated oxides of nitrogen need only be returned in part to the Glover tower for denitration. The bulk can be passed to a silicon iron denitrating column, and the nitrogen oxides recovered in the form of nitric acid, 60 per cent HNO_3 . The absorption towers for such plant need only be relatively small, as the nitric acid vapours are free from diluent gases.

The process can be varied at will, so as to produce a negligible quantity of nitric acid and a considerable quantity of sulphuric acid, under intensive conditions; or units contemplating the manufacture of varying proportions of sulphuric and nitric acids can be arranged.

For the production of sulphuric acid, the plant will consist of an ammonia oxidation unit with Glover tower, a tower for the regeneration of nitric oxides, and one or two suitable Gay Lussac towers.

For the production of sulphuric and nitric acids, the plant will comprise ammonia oxidation units (in which concentrated ammonia liquor, 25 per cent, can be used), a special form of sulphuric acid plant embodying Glover tower, a tower for the regeneration of nitric oxides and Gay Lussac towers, and finally denitration plant with absorption towers for the recovery of the oxides of nitrogen as nitric acid, 60 per cent HNO_3 .

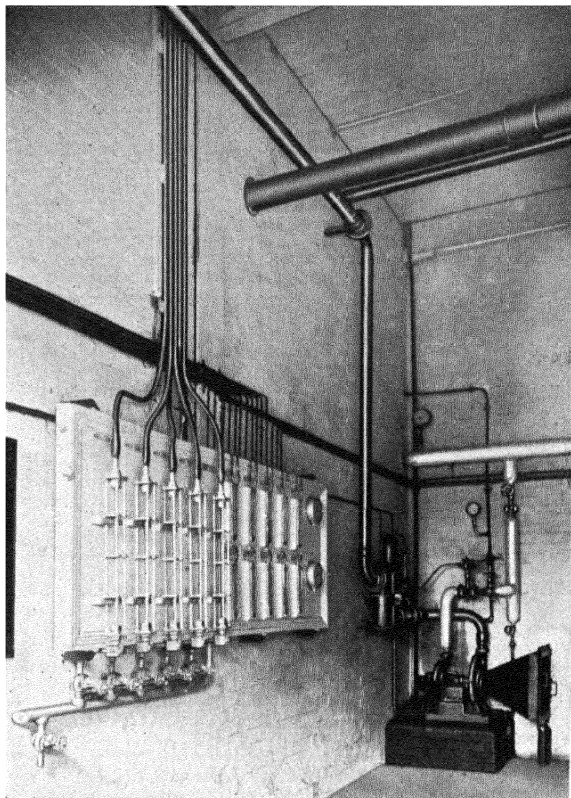


FIG. 159.—MEASURING DEVICES (ROTA REGULATORS) FOR AMMONIA OXIDATION UNITS

Fig. 160 shows a view of a plant producing daily 40 tons of sulphuric acid (monohydrate) and 20 tons of nitric acid, 100 per cent. Fig. 158 shows the converters in connection with this plant. It is peculiarly applicable to the utilisation of concentrated ammonia liquor and concentrated gas liquor, and would admit of a variety of nitrogenous and other fertilisers being manufactured under such conditions of flexibility and economy as can hardly be attained by other processes.

A complete superphosphate factory is shown in Fig. 163. This includes plant for the manufacture of 40,000 tons per year of calcium superphosphate, based on 280 working days per annum, of 16 hours each. It incorporates the necessary plant for the manufacture of sulphuric acid, of the Gaillard-Parrish type, concerning the features of which a detailed description has just been given. Provision is also made for the de-arsenication of a small predetermined quantity of the sulphuric acid, as this is required for special purposes. The site provides for the raw materials and finished goods to be transported by sea or rail.

The phosphate rock is conveyed from the side of the quay by an underground band conveyor, which delivers to a vertical elevator at the end of the phosphate store. The store is shown in section E—E, and it will be noted that it is of parabolic section, built in ferroconcrete. This design is to be commended, as it represents the most economical construction, advantage being taken of practically the whole of the free space. The elevator referred to delivers to a band conveyor, which runs the full length of the store in a superimposed tunnel. It is provided with a throw-off carriage, which discharges the phosphate rock at any desired point, and can fill the store from end to end. The store, when filled, holds 7,000 tons. The phosphate storage plant is capable of handling 40 tons per hour, and is automatic from the time the phosphate leaves the ship until it is discharged in the store.

The grinding plant is shown in sections A—A and B—B. In this plant the phosphate rock calls for no preliminary crushing. The rock is brought from the store to the grinding plant by means of a Fordson shovel. This equipment gathers a load of half a ton, and travels forward and delivers into a receiving hopper at ground level. The phosphate rock is elevated to a silo, which holds approximately 20 tons. From this storage bin it is automatically fed to the grinding plant at a predetermined rate. The grinding equipment consists of a ring-roll mill, working in conjunction with mechanical air separation equipment, which has been the subject of a detailed description in Chapter IV.

The grinding plant has a capacity of 6 to 8 tons per hour, when grinding to a fineness of 80 per cent through 100 mesh B.S.S.

The ground phosphate is delivered to a silo having a capacity of approximately 100 tons. This provides a reserve, should a temporary breakdown occur in the grinding unit. The ground phosphate is withdrawn from the silo by means of a bulk extractor, and elevated to the mixing equipment disposed over a Broadfield continuous den. The features of this special den have been

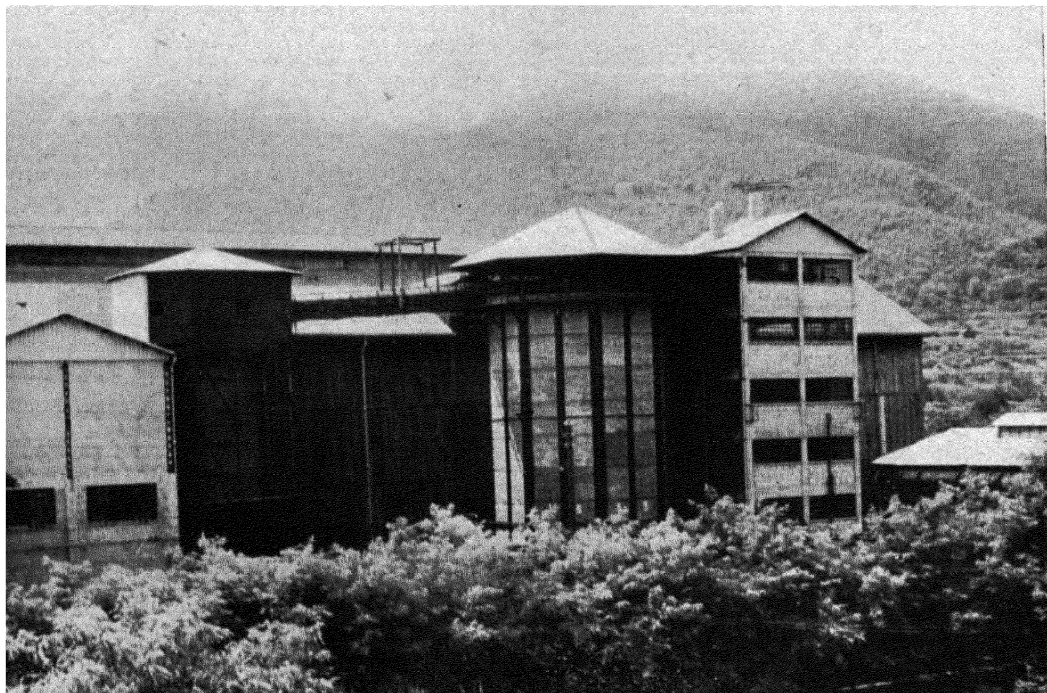


FIG. 160.--GENERAL VIEW OF KACHKAROFF M.-P. COMBINED SULPHURIC AND NITRIC ACID PLANT

described fully in Chapter VII. This plant produces 10 tons per hour of calcium superphosphate, or 160 tons per working day. The superphosphate, as it is sliced, is discharged to a band conveyor, which delivers from a height of approximately 15 feet to the floor of the superphosphate store. It is then gathered by an electric overhead crane having a grab bucket, and deposited at any point along the store where it may be required.

It will be observed, from the detailed outline of the factory, that about the centre of the superphosphate store, and along the side adjacent to the railway and the quay, two superphosphate dressing units are situated. This equipment is described in detail in Chapter XI. Each unit will handle and dress 20 tons per hour. It is possible, therefore, during rush periods, to ship about 460 tons in a working day. The superphosphate store holds approximately 15,000 tons, without encroaching on the dressing units. These are fed by means of an overhead electric crane. The layout of the superphosphate plant is such that the materials pass through the factory in one direction only: thus space and labour are economised.

When the annual output is 40,000 tons, the power consumption should not exceed eight electrical units per ton of calcium superphosphate produced, and the total cost of labour employed on all operations (1938) should not exceed 1s. per ton on the final product, delivered into bags.

✓ *The Management of a Superphosphate Factory*

Management training is now an important subject in certain curricula. It is generally conceded that organised instruction can provide a satisfactory basis of knowledge, calculated to develop personality and individual capacity for management.

Speaking broadly, the managers of the future will not only possess fundamental technical and practical knowledge, but they will have been trained in the fundamentals necessary to equip them for the responsibility of management.

Apart from the technical aspect of management associated with production, distribution and development, and irrespective of the functions of the general manager, where such an appointment

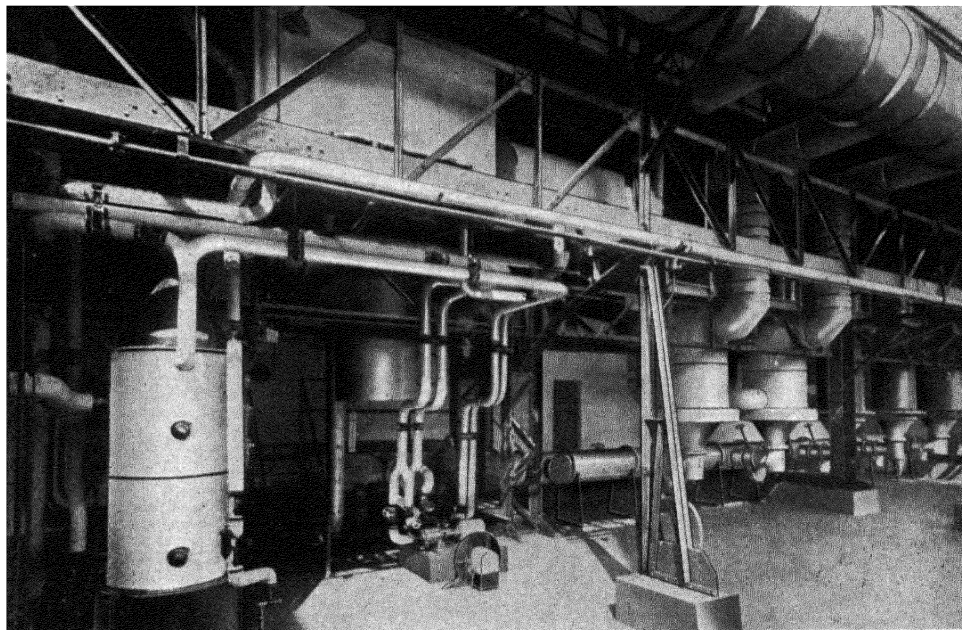


FIG. 161. — CONVERTERS (AMMONIA-OXIDATION) OF A KACHKAROFF M.-P. SULPHURIC-NITRIC ACID PLANT

is made, the normal affairs of a company, as regards its relations with the outside world, are generally in the hands of its directors and secretary. The provisions of the Companies Act of 1929 outlined the usual duties of directors. Directors are officers and servants of the company, despite the fact that they are responsible for its destiny. Their position is alike that of trustees and agents,

The secretary is an agent of the company, for the particular duties he is deputed to perform and the executive officer of the directors, to whom he is responsible. He must carry out the directors' instructions, and pass such to the staff: he must see that the company fulfils all legal requirements, and that the provisions of the Memorandum and Articles of Association are complied with. He must prepare the agenda for directors' and general meetings: see that the statistical books are properly kept, satisfy himself that transfers are in order before submission to the directors to be passed, and (usually) must sign or countersign cheques, share certificates, dividend warrants, and similar documents, after having verified them, before sealing and/or signature by the directors.

Fertiliser companies may be such that they can warrant a large staff, and have an organisation such as is represented by diagram Fig. 162. Or they may be of such limited dimensions that an elaborate staff is impossible, and the head has to act as the general factotum, being responsible for purchases, sales, technical management, accountancy matters, secretarial work, and indeed general development. Such a man must possess not only a knowledge of the technique of management, but also those qualities which are normally summarised in the words "personality" and "character." Purely intellectual attainments and the study and mastery of the technique of management is not everything. It may be a *new* factor in management, but the older ones such as character, ability to win confidence, powers of decision, enthusiasm, fine judgment, leadership, and a lively sense of justice still count as much as—if not more than—hitherto.

But one must assume that the right man (or men) is (or are) in the right place, and that he is (or they are) faced with the conduct of a fertiliser company. What seems pre-eminently clear is that the successful conduct of any business to-day depends on planning ahead, and on the adoption of budgetary control, which may be said to be "a highly developed method of co-ordinating working to a plan of estimates, based on the fullest information available, interlocking these systems into a budget, and generally checking-up results against quotas set". This calls for combining experience with judgment of facts, and of integrating such experience and judgment to secure the highest degree of accuracy.

In connection with such management, industrial accounting, principles of costing and estimating control of expenditure and statistics and graphs, are some of the modern aspects. To deal with these phases separately, and at all fully, may involve much more time and space than are available.

Costing covers the application of accounting results of all expenditure for the purpose of arriving at the inclusive cost per unit of saleable product. The unit in the fertiliser trade is initially the cost per ton of the manufacture of calcium superphosphate, and secondly, the cost of the production of various N P K. mixtures prepared for specific purposes. In the first case, the costs of the manufacture of sulphuric acid and calcium superphosphate enter largely into the determination. In the second case, the blending of nitrogenous, phosphatic and potassic fertilisers in predetermined proportions, and the cost of conditioning such blends or mixtures, or otherwise granulating them, which may be effected by several methods, are essentially the items calling for determination.

Costing and Estimating—Estimating runs parallel in form with costing. It represents an attempt to forecast the inclusive cost (per unit of saleable product), in the light of previous experience, so far as the costing system can provide appropriate data. Where comparable cost data are not available, it is necessary to resort to estimates based on technical investigations and calculations. These estimates in pre-war years were haphazard and unreliable, as many have good reason to know.

Cost accounting, in its more recent manifestations, covers both the field of industrial accounting and costing in the more specific sense used above. Stress of competition has necessitated the evolution of more exact methods of determining what the cost of a unit of production is, whether it be a ton of coal or a ton of calcium superphosphate, or a thousand eggs, or a ton of pig iron, or a motor car. The cruder methods of two or three decades ago are now no longer tolerable.

At the most modern works the cost sheets must balance not only with the accounts revealed by industrial accounting, but with the reports of chemical efficiencies. This represents the culmination of a system of correlation and verification, which takes some years to develop. But for a chemical manufacturing undertaking it can be commended.

Without further comment the technical data and cost sheet relating to the manufacture of calcium superphosphate will be given.

Technical Data Concerning the Manufacture of Calcium Superphosphate

M'Dilla Superphosphate.

184 lb. of M'Dilla phosphate	} Supplied per minute to a Broadfield den.
162 lb. of sulphuric acid,	
127 ² Tw. (71.57 % H ₂ SO ₄)	

Analysis of the Phosphate Rock.

Moisture	3.6 per cent.
Tribasic phosphate of lime, Ca ₃ P ₂ O ₈	68.0 "
Oxides of iron and alumina	1.5 "
Carbonate of lime	12.7 "

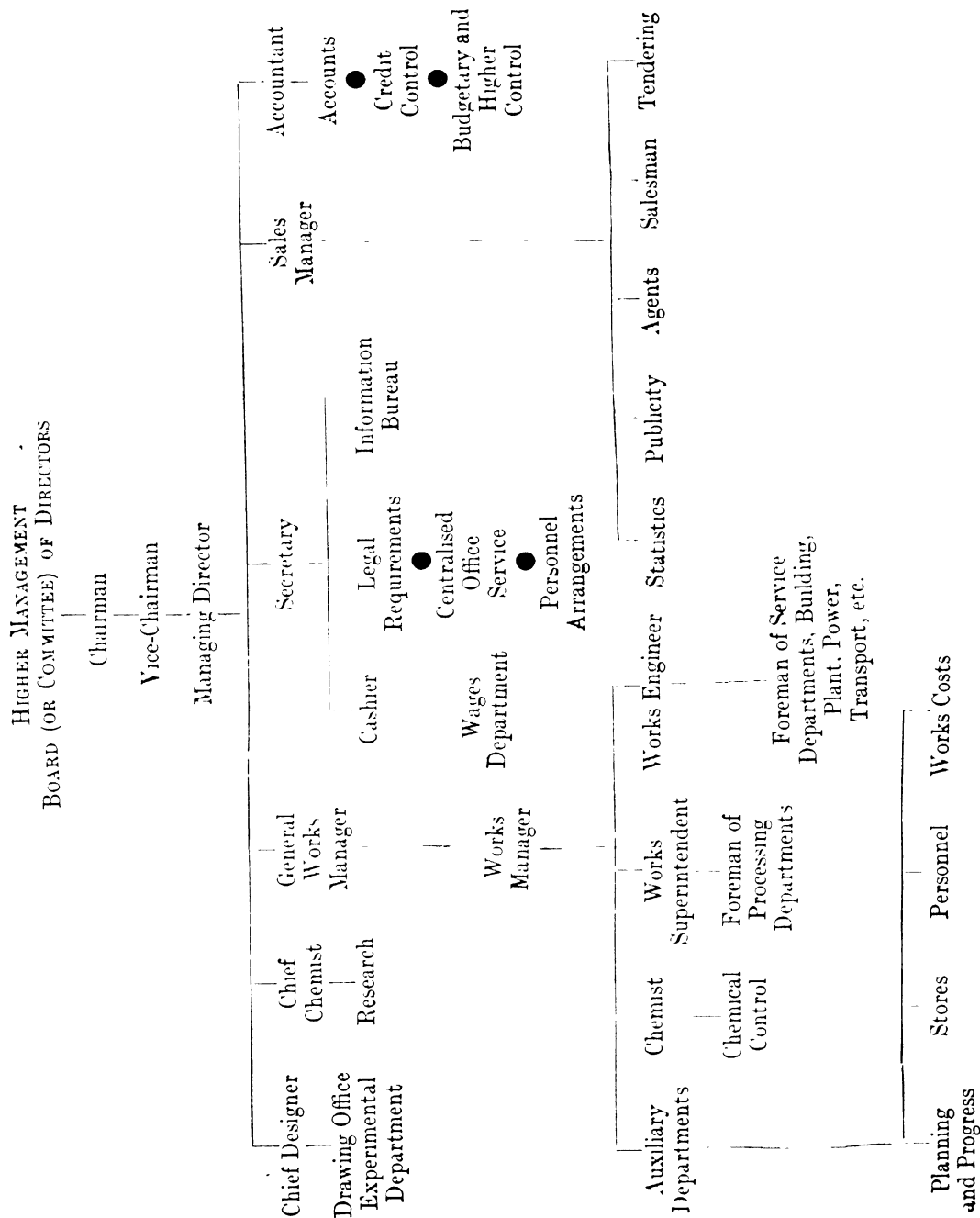


Fig 162—ORGANISATION CHART AS APPLYING TO A LARGE FERTILISER COMPANY

TABLE 58

Cost Sheet Relating to the Manufacture of Calcium Superphosphate
(15 per cent P_2O_5 or 32.75 per cent $Ca_3P_2O_8$)

	Cost per unit of				
	Per ton £ s d	P ₂ O ₅ (15%) s d	Ca ₃ P ₂ O ₈ (32.75%) s d	Percentage	
RAW MATERIALS					
1. 1,193 lb. of phosphate rock 10.65 cwt at 5½d per unit plus 1d per unit extra freight 36s 1½d per ton	19 3	1 3.4	7.05	38.8	
2. 1,057 lb. sulphuric acid (71.57%) 1,080 lb. (70%) 9.64 cwt at 29s 6d per ton	14 3	1 1.4	5.22	28.8	
3. Grinding phosphate rock	1 13 6	2 2.8	1 0.27	67.6	
(a) 7½ units of electricity at 1d 2s 6d	s d 7½				
(b) 2 men at 1s 3d 8 tons/hour	4				
(c) Repairs and maintenance, say	2				
To grinding of 10.5 cwt at 1s 1½d per ton	1 1½				
4. Mixing and discharge to continuous den and cutting	7	0.5	0.21	1.1	
(a) Labour 1 man (mixing floor) 1 man (discharging) 1 man (ground phosphate store)	s d 1 3 1 3 1 3				
	3 9				
3s 9d. 10 tons/hour	s d 4½				
(b) Power 20 h p at 1d 10 tons/hour	2				
(c) Repairs and maintenance materials and labour	3				
5. Screening and pulverising oversize, bagging and sewing	9½	0.6	0.25	1.6	
(a) Labour Crane-man 2 men bagging 2 men sewing	s d 1 3 2 6 2 6				
(b) Power 20 h p at 1d	1 8				
7s. 11d. 10 tons/hour	7 11				
6. Power other than already specified	9½	0.6	0.25	1.6	
7. Cost of bringing phosphate rock to grinding plant 10.65 cwt. at 9d. per ton, say	4	0.3	0.12	0.6	
	5	0.3	0.15	0.8	
	1 16 5	2 5.1	1 1.25	73.3	
8. Chemical supervision, say	4	0.3	0.15	0.6	
9. Engineering supervision, say	6	0.4	0.18	1.0	
10. Other repairs and maintenance	9	0.6	0.27	1.5	
11. Bags (10 to the ton) and string at say 5d	4 2	3.3	1.51	8.2	
12. Lighting and heating of lobbies and canteens	6	0.4	0.18	1.0	
13. Rates, rent and insurance (wages and fire)	1 0	0.9	0.40	2.1	
14. General on-costs	2 6	2.0	0.90	4.9	
15. Interest (5%) and depreciation (7½%)					
= 12½% on capital	£ s d				
less (sulphuric acid plant)	125,000 0 0				
	75,000 0 0				
£8,250	50,000 0 0				
12½% =	2 6	2.0	0.90	4.9	
50,000 tons					
16. Contingent expenses, 2½% on Items 1 to 15, say	1 4	1.1	0.49	2.5	
COST PER TON OF CALCIUM SUPERPHOSPHATE	2 10 0	3 4.1	1 6.23	100.0	

It is difficult to prepare a cost sheet for the manufacture of calcium superphosphate at the present time (1945). There is reason to know that the superphosphate industry is being subsidised both in respect of (a) phosphate rock and (b) sulphuric acid, 70 per cent, and moreover, the selling price of calcium superphosphate, 18 per cent P_2O_5 , has been increased from £3 10s. per ton in 1939 to £5 8s. 9d. per ton in 1945. The cost of freight on phosphate rock has conceivably increased by 400 per cent since 1939, and even to-day it is nearly three times what it was in 1939, and there seems to be little hope that it will be less than twice the 1939 rate for some considerable time, having regard to the fact that (a) the cost of fuel and/or oil has increased considerably, (b) wages have sensibly advanced and (c) the capital cost of ships to-day must be appreciably more than what obtained in 1939. It is obvious, therefore, that without a substantial subsidy the calcium superphosphate industry could not have continued to operate economically.

Analysis of Calcium Superphosphate

Age of superphosphate	12 days per cent.	17 days per cent.	24 days per cent.	34 days per cent.
Moisture	13.13	13.03	12.82	11.59
Total P ₂ O ₅	16.58	16.56	16.79	16.82
Equals tribasic phosphate of lime, Ca ₃ P ₂ O ₈	36.22	36.16	36.68	36.75
Water-soluble P ₂ O ₅	15.10	15.45	15.40	15.50
Equals tribasic phosphate of lime, Ca ₃ P ₂ O ₈	32.97	33.74	33.63	33.85
Free acid, as P ₂ O ₅	2.84	2.48	2.13	2.31

Deductions from Analyses

1. Percentage loss of Ca ₃ P ₂ O ₈	8.90	6.60	8.31	7.90
2. Efficiency of recovery	91.10	93.40	91.69	92.10
3. Production ratio : Superphosphate : Phosphate rock (100)	187	188	186.4	*186.2
Feed of phosphate rock per minute		184 lb.		
4. Production of calcium superphosphate per hour		184 lb. × 60 (mins./hr.) × *186.2 = 9.175 tons per hour.		

Concerning the cost sheet on page 251, it should be remarked that an attempt has been made to place the determination of the raw materials required in the production of a ton of calcium superphosphate of a given quality on a definite basis. Hitherto it was felt that there may have been an element of conjecture in arriving at the quantities used. True, in a normal way, the works manager will issue a return, from details furnished him, that a certain quantity of phosphate rock and a certain quantity of sulphuric acid have been used in the production of "X" quantity of calcium superphosphate of a given quality.

The question arises: How far can careful analyses of (a) phosphate rock, and (b) the calcium superphosphate, constitute a check on the quantities actually used? After all, in the interests of accuracy, check determinations are desirable, otherwise a certain degree of laxity may arise. What many chemical and fertiliser works have failed to appreciate in the past is the importance of accurate weighings.

From the technical data sheet, the feed per minute to the mixer of the continuous den is given as 184 lb. of phosphate rock and 162 lb. of sulphuric acid (71.57 per cent H₂SO₄).

184 lb. phosphate rock.

162 lb. sulphuric acid (71.57 per cent H₂SO₄).

The production ratio is 1.862; thus,

184 lb. of phosphate rock will produce

$$184 \text{ lb.} \times 1.862$$

$$= 342.6 \text{ lb. of calcium superphosphate.}$$

Therefore $\frac{2240 \text{ lb./ton}}{342.6 \text{ lb.}} = 6.5382$ (factor).

184 lb. of phosphate rock × 6.5382 = 1193 lb.

$$= 10.65 \text{ cwt.}$$

162 lb. sulphuric acid (71.57 per cent) × 6.5382

$$= 1057 \text{ lb. (71.57 per cent), or } 1080 \text{ lb. (9.64 cwt.) of } 70 \text{ per cent H}_2\text{SO}_4.$$

Electric power can only be accurately assessed by meter-reading over a period, during which there has been a definite quantity of calcium superphosphate made and a definite quantity loaded. The power requirements of a calcium superphosphate works of the size contemplated by the above figures must vary with different works, their location, and modernity or otherwise. The following statement would appear to set out the power units, under economic conditions, of a plant capable of producing 50,000 tons of calcium superphosphate per annum :

TABLE 59

Index.	Purpose.	H.P.	Capacity of unit.
A	Grinding unit	50	8 tons per hour.
B	Mixing, continuous den and cutting	20	10 „ „
C	Screening, disintegrating oversize, bagging and sewing	20	10 „ „
D	Fan for condensers	9	
E	Robson shovel	10	
F	Overhead crane	50	
G	Crane on wharf	25	
H	Elevators for phosphate rock (grinding plant)	10	
	Elevators for phosphate rock to mixer	10	
	Two elevators for screening-bagging plant	16	
		220	

What the minimum consumption of power should be per ton of calcium superphosphate manufactured and packed into bags depends upon many factors, but the cost sheet is helpful in this regard. It must be remembered that all the power units are not operated continuously—indeed, that many of them only work for a relatively short time, and deal with sensible quantities during that time.

Percentage Cost of Raw Materials.—What the cost sheet reveals in a striking way is that 67.6 per cent of the manufacturing cost of calcium superphosphate concerns the raw materials. If it is desired, therefore, to reduce the cost of manufacture, one must (a) buy the phosphate rock to better advantage, or (b) must manufacture the sulphuric acid at a cheaper price, or (c) otherwise effect economies on the quantities of raw materials used; in other words, one must aim at a higher efficiency than that on which the cost sheet is based, which is typical, for the most part, of the efficiencies of many superphosphate works to-day.

It should be remarked that the price of sulphuric acid contemplates repairs and maintenance, chemical and engineering supervision, on-cost charges, and interest (5 per cent), and depreciation (7½ per cent).

We have often been asked. What does a 1d. per unit of sulphur in pyrites represent, per ton of calcium superphosphate?

512 lb. of sulphur is theoretically required per ton of 70 per cent acid, or in other words 22.86 units of sulphur.

If the price of sulphur is increased by 1d. per unit, this will represent say 1s. 11d. per ton increase in the price of 70 per cent acid.

Reference to the cost sheet relating to the manufacture of calcium superphosphate will show that 9.64 cwt. of 70 per cent is required per ton of calcium superphosphate containing 15 per cent P_2O_5 , or 32.75 per cent $Ca_3P_2O_8$.

Therefore, the effect of increasing the price of sulphur in pyrites by 1d. per unit would represent :

- 9.64 cwt, at 1s. 11d. per ton of 70 per cent acid -
- 11d. per ton of calcium superphosphate, 15 per cent P_2O_5 , or say $\frac{3}{4}$ d. per unit of P_2O_5 .

We should like to pursue the analysis of costs still further, but space, unfortunately, does not admit.

We give below a cost sheet, showing how the figure of 29s. 6d. per ton of 70 per cent sulphuric acid has been arrived at.

Estimated cost of manufacturing sulphuric acid of 50° Bé., 106° Tw., 62.53 per cent H_2SO_4 , from Pyrites, by the Gaillard-Parrish liquid phase system

	\pounds		s.	d.
1. 9.3 cwt. of pyrites containing 50 per cent of sulphur, at 6d. per unit =25s. per ton		11		8
2. $3\frac{1}{2}$ lb. of ammonia at 5s. per unit of 22.4 lb.				9 $\frac{1}{2}$
3. Labour for one unit of plant, producing $62\frac{1}{2}$ tons of 50° Bé. acid per day. 15 men at 10s. per day				
150s.				
$62\frac{1}{2}$ tons		2		6
4. Total horse power required, 36 h.p. at 0.4d. per h.p. hour				
$37\frac{1}{2} \times 24$ hrs. \times 1d. = \pounds 3 15s.				
\pounds 3 15s.				
$62\frac{1}{2}$ tons		1		2 $\frac{1}{2}$
5. Water, 2,000 gallons per hour at 6d. per 1,000 gallons. (This assumes the use of a Premier Cooler. thus only replenishment water has to be charged)				
1s. \times 24 hrs.				4
$62\frac{1}{2}$ tons				
6. Repairs and maintenance : materials and labour		2		0
7. One chemical plumber, at \pounds 5 per week				
16s 6d. per day				
$62\frac{1}{2}$ tons				3
8. Part Chemist and part Engineer at \pounds 600 per year				
$\frac{\pounds 600}{300 \text{ days}} = \frac{\pounds 2}{62\frac{1}{2} \text{ tons}}$				7 $\frac{1}{2}$
Prime cost		19		4 $\frac{1}{2}$
9. Interest on capital at 5 per cent				
5 per cent of $\pounds 44,427$ 10s. = \pounds 2,221.35				
$\frac{\pounds 2,221.35}{20,625 \text{ tons per annum}}$				
say		2		2
10. Depreciation, at 7 $\frac{1}{2}$ per cent				3 3
11. Overhead charges				1 6
TOTAL COST PER TON OF 50° BÉ. ACID		1	6	3 $\frac{1}{2}$
Therefore 70 per cent sulphuric acid =		1	9	6

The above cost sheet, in May 1945, will need to be modified as follows:

1. Pyrites, say 1s. 3d. per unit of sulphur, although it is impossible to purchase to-day (May 1945) at this price.
2. Liquor ammonia, 25 per cent, costs, in May 1945, 6s. 9d. per unit, delivered.
3. Shift workers in London are receiving 16s. 8d. per shift of 8 hours.
4. ———
5. ———

6. Repairs and maintenance (materials and labour) should be doubled.
7. Chemical plumbers' wages are of the order of £6 10s. per week.
8. Chemists' and engineers' salaries should be increased by £150 per annum.
9. ———
10. The income-tax authorities allow 15 per cent, plus one-fifth depreciation allowance, calculated on diminishing balances for the major portion of the plant. This may be regarded as representing approximately 9 per cent on a fixed capital value, of which details are given on page 252.
11. Overheads, or general on-costs, should be doubled, because under this item one has to contemplate rates, insurance (general, fire and workmen's compensation), laboratory and workshop expenses, part welfare, first aid and fire appliance expenses, maintenance of repair shops and stores, upkeep of roads, rails, drains, fences, etc. The latter may be regarded as constituting one part of general on-costs: on the other hand, there are the purely administrative items, such as rent, rates and taxes, head office salaries and insurances, head office facilities (stationery, telephone, etc.) and a portion of directors' fees.

Subject to the above modifications, the subsequent text about the cost of sulphuric acid relates to the conditions obtaining in 1939, and must be corrected in accordance with the current (1945) indications.

Little has been published about manufacturing costs of sulphuric acid. Apart from odd references here and there, it would appear that the first publication of any importance—and this, indeed, was a significant communication—was *Notes on Sulphuric Acid Manufacture*, by the Department of Explosives Supply, issued in June, 1917. The figures incorporated in that communication, apart from the basic technical calculations, are not of much value to-day, because (a) the price of raw materials, (b) costs of labour, and (c) other items of importance affecting cost, have changed materially. Further, relative efficiencies of the chamber and contact processes have altered, as indeed has the capital expenditure involved in these two forms of plant. Thus, fresh computations are necessary, if anything approaching reliable comparisons are to be instituted.

The National Sulphuric Acid Association Ltd. has, of course, continued to interest itself keenly in costs of manufacturing sulphuric acid. A Cost Committee constitutes part of its organisation, and cost figures are circulated privately among its members.

But in 1937 a book on *The Economics of the Sulphuric Acid Industry*, by Theodore J. Kreps, was published by the Stamford University Press, California (London publishers, Humphrey Milford, Oxford University Press). It is a book of absorbing interest, and one which has not received the notice that it deserves. It is a monograph comprising one of the results of a programme of research initiated more than ten years ago at the suggestion, and under the direction, of Prof. F. W. Taussig, of Harvard University. The author states that under professorial guidance an inquiry was begun into the economic problems raised by the penetration of chemical processes into industrial technology, and this at a time when the United States economic literature lacked even short written accounts of such important branches of the chemical industry as those manufacturing sulphuric acid, alkali, or coal tar dyestuffs.

The question arises, are University graduates equipped with fundamental knowledge, but little practical experience, the best envoys to start an investigation of this character? Are they likely to get at the fundamentals, even after visiting chemical plants, interviewing executives, and making a field study? Mr. Kreps makes clear that the Bureau of International Research at Harvard University granted him a further appointment as Laura Spelman Rockefeller Fellow, for the academic year of 1928—29, which he spent collecting materials abroad, especially in England and Germany. He remarks that the unlimited access afforded him at this time by the Interessengemeinschaft Farbenindustrie Aktiengesellschaft to their extraordinarily complete chemical library at Höchst-am-Main was especially helpful. Whatever views one may form about this contribution, it is one that should be studied, because there is a wealth of information available, that is bound not only to invite further inquiry, but which will prove provocative of further thought on the aspects with which it deals.

It should be remarked that one ton of 70 per cent sulphuric acid should be produced by 512 lb. of sulphur. In 9.3 cwt. of pyrites, 50 per cent sulphur, there are 520.8 lb. of sulphur, so that an overall efficiency of 98.4 per cent is contemplated. This will call for the highest possible burning efficiency, as well as conversion efficiency: indeed, except the pyrites are of special quality, it is doubtful whether such an overall efficiency can be attained. Generally speaking, overall efficiencies of 96 per cent represent an average, and keen chemical and technical supervision has to be exercised in order to ensure this.

Equally, experts may doubt whether, over a period of say 20 years, repairs and maintenance can be effected for 2s. per ton, taking the depreciation figure into consideration. Glover and Gay Lussac towers are known to have served for practically twenty years, and the steel construction, after that time, has been found to be almost as good as new. Only the leadwork, the lining and

packing materials, the distributors, the Glover coolers, stalk and connecting pipe, have called for repairs and/or renewal. If the plants are operated at reasonably full output throughout the year (it needs consummate management to ensure this) it will be found that the figures for repairs and maintenance, and depreciation, are not wide of the mark.

Comparative Costs of Sulfuric Acid, Chamber versus Contact Process
(Dollars per ton of sulphuric acid, 100 per cent acid basis)*

Item of expense.	Chamber process.		Contact process.	
	Dollars per ton	Per-centage.	Dollars per ton.	Per-centage.
Factory cost :				
Sulfur, 677 lb.	\$7.00	51.85	\$7.02 (684 lb.)	52.00
Niter (as anhydrous ammonia) 5 lb.48	3.56	---	---
Water, steam and supplies, 2,500 gals.23	1.70	.25 (5,000 gals.)	1.85
Power, 15 kw. hr.32	2.37	.37 (25 kw. hr.)	2.74
Repairs40	2.96	.31	2.30
Labor, 1.1 man hour58	4.30	.58 (1.1 man hr.)	4.30
Plant administration48	3.56	.26	1.93
Taxes, depreciation, etc., on \$230,000 unit of 50 tons per day capacity51	3.78	1.21	8.96
Total factory cost	\$10.00	74.08	\$10.00	74.08
Distribution cost :				
General and administration50	3.70	.50	3.70
Sales cost	1.00	7.41	1.00	7.41
Containers, etc50	3.70	.50	3.70
Profit	1.50	11.11	1.50	11.11
Total of all items	\$13.50†	100.00	\$13.50†	100.00

* Computed from data furnished by the editors of *Chemical and Metallurgical Engineering*.

† Authors' note: Based on 4.68 dollars to the £ sterling, this represents:

	100 per cent H ₂ SO ₄	£2 17s. 8d. per ton
	70 per cent H ₂ SO ₄	£2 0s. 4d. per ton.
or at the factory:	100 per cent H ₂ SO ₄	£2 2s. 9d. per ton.
	70 per cent H ₂ SO ₄	£1 10s. 0d. per ton.

It should be noted that the above converted prices apply (presumably) only to one ton of 2000 lb. The price expressed in terms of an English ton of 2240 lb. would be.

	100 per cent H ₂ SO ₄	£3 2s. 11d.
	70 per cent H ₂ SO ₄	£2 5s. 2d.
or at the factory:	100 per cent H ₂ SO ₄	£2 7s. 10d.
	70 per cent H ₂ SO ₄	£1 13s. 6d.

N.B. -1945 conditions: Chamber sulphuric acid plants, under the conditions obtaining in 1945, can produce sulphuric acid at a cheaper price than the contact sulphuric acid plants, and basing on pyrites at 1s. 3d. per unit and sulphur at say, 1s. 7d. per unit, chamber plants should be able to produce the equivalent of 100 per cent H₂SO₄ at £4 12s. 6d. per ton, and contact plants at £4 17s. 6d. per ton.

The cost sheet does not contemplate the renewal of platinum or platinum-rhodium gauzes, or repairs to the ammonia oxidation plant. But these expenses are covered by 2d. per ton.

Sixpence per unit for the sulphur in pyrites covers delivery into silos, and loading of the cinders to barge or ship. This may be regarded as too low a figure. Perhaps to-day (1938) 6½d. per unit of sulphur of pyrites may more nearly represent the overall cost.

Whether overhead charges can be covered by 1s. 6d. per ton is doubtful, particularly where a large organisation exists, and where modern welfare facilities, sickness and unemployment funds, ambulance, holidays with pay and part superannuation contributions by the firm, as distinct from the staff and workers, are provided.

Not infrequently we have been challenged about the cost of manufacturing sulphuric acid, 70 per cent, and have had to cope judiciously with dogmatic assertions that acid of this strength can be made for 20s. to 25s. per ton. Obviously, statements of this kind need only be analysed, as we have attempted to do above, in relation to a reasonably reliable cost sheet, to merit their own condemnation.

While on the subject of the cost of manufacture of sulphuric acid we should remark that we have often been asked to give respective costs of manufacture of sulphuric acid by (a) the contact process and (b) the chamber process. These costs vary widely, and are determined by varying factors. It is well-nigh impossible to get strictly comparable figures. But in this connection we can do better than furnish the latest modern comparison, which is culled from *The Economics of the Sulphuric Acid Industry*, by Kreps. We give his observations, as well as the comparative costs, so that readers may have regard to his views, as well as those we have expressed. Kreps has observed, on this subject :

“. . . The task of summarising the competitive status of the contact process as against the chamber process is one of the greatest difficulty. Enormous variations exist in costs of plants using the same process, even those using the same equipment and the same general technical supervision. At best only a general or idealised picture can be given. This I have endeavored to present in the accompanying table. It assumes roughly the present (1937) level of prices and better-than-average technical efficiency. The contact plant here envisaged is one of the more modern kinds, with a capacity of 50 tons per day 100 per cent acid, using vanadium catalyst and processing the raw gases.

“The most important differences between the two processes shown by the table occur in the items of plant administration, taxes, and depreciation. The contact plant, costing roughly the same to build, wears out more quickly. It uses more water and slightly more power, but no niter. Other expenses are practically identical. Total costs are likewise about the same.”

The relative cost figures furnished by Kreps are not beyond criticism. Nothing appears to be included in the cost sheet for contact sulphuric acid for replenishment or renewal of the catalyst. One of the authors has operated contact plants for several years, and is aware that renewal of catalysts has to be undertaken from time to time, and that a definite charge should be made in this connection. Moreover, the contact process is never operated with the same overall efficiency as the chamber process. On this subject the Chief Alkali Inspector, Mr. W. A. Damon, B.Sc., has made the following observations :

“. . . The tendency to prefer the contact system needs consideration, in view of the fact that, unless some form of scrubbing is applied, the escapes are higher than those from chamber plants. Where scrubbing is practised, the bisulphate method is generally employed, but the demand for this product is limited and the means is not in all instances a practicable one to adopt. The escape is an index of the efficiency of conversion and subsequent absorption (principally the former) but, in spite of the design of convertors being continually improved and more satisfactory masses being produced, the escapes remain relatively high. Chemists both in this country and abroad are actively engaged in seeking a method whereby sulphur dioxide in low concentrations may be economically recovered as a saleable product.

“The average of escapes from plants where no scrubbing is practised was 3.64 grains and that from plants where scrubbing is practised was 0.58 grain. The significance of these figures will be readily appreciated.”

It is difficult to understand why there should be such a predilection for vanadium catalysts. Platinum catalyst, for the conversion of sulphur dioxide to sulphur trioxide, proved of admirable service in war-time plants, and the high scrap value of the used material is certainly an important consideration. In United States plants, per ton/day of 100 per cent sulphuric acid, 5.5 to 7 oz. troy of platinised asbestos or platinised magnesium sulphate is now required, and only 1.5 to 2.1 oz. of platinised silica gel, as contrasted with war-time requirements of 13 to 16 oz. These are figures that should give acid manufacturers to think.

Space does not allow us to enter into important aspects concerning costs, and control of costs of compound manures, whether conditioned or granulated. But in all cases it is preferable to express costs in terms of units of P_2O_5 , K_2O , and N_2 .

If the sale of compound fertilisers is to pay, as indeed is generally the case, it is necessary to buy sulphate of potash, or chloride of potash, or potash salts, on advantageous terms, and equally to manufacture sulphate of ammonia at an economic price. Where plant does not exist for such manufacture, sulphate of ammonia must be bought to advantage.

In any case, there is need for careful chemical supervision in the compounding of fertilisers, and in the analysis of the final products. No less important is the necessity for accurate cost accountancy, so that the sales manager knows at what price he can dispose of the various products, in order to ensure to his company a reasonable predetermined profit.

But management must not alone concern itself with costs, however vital these may be. A fertiliser company must determine on a policy of service to their clients, - indeed, everything must be directed to this end. Given service to clients, one can anticipate a continuance— and perhaps an increasing volume—of orders. No effort should be spared in ensuring complete satisfaction to clients. The feeling should be engendered that the fertiliser company is ever ready to give them assistance in whatever aspect it may be needed.

And equally, consideration should be given to the staff and workmen. They should be made to feel that their welfare is ever a matter of careful consideration. Where the business is large enough there should be a personnel department, and the feeling should not be permitted to arise that this is an encroachment on the authority of the managers and supervisors. The acid test is the benefit that such a department can exert on the organisation as a whole. Individual attention to long-term interest in the business, and to all those associated with its demands, can be fostered only by a personnel department of the right kind, properly initiated and run.

That there is a human factor in business to-day goes without saying, and that this must be rightly cultivated is self-evident.

APPENDIX

TABLE 60

Specific Heats of Gases

	Constant pressure 0° 100° C.	Constant volume.	Ratio K.
Air	0.237	0.163/100° C.	1.403
Ammonia	0.520	0.390/18° C.	1.28
Carbon Dioxide	0.209	0.151/15° C.	1.26
Carbon Monoxide	0.242	0.168/-	1.41
Chlorine	0.124	0.083/18° C.	1.34
Hydrochloric Acid	0.187	—	1.42
Hydrogen	3.410	2.40/50° C.	1.41
Methane	0.593	—	1.31
Nitric Oxide	0.231	—	1.39
Nitrogen	0.245	0.168/15° C.	1.40
Oxygen	0.217	0.183/0 2,100° C.	1.40
Sulphur Dioxide	0.154	—	1.26
Water Vapour	0.454	0.340/100° C.	1.33

TABLE 61

Comparison of Hydrometer Degrees Twaddell and Baumé with the Specific Gravities for Liquids heavier than Water

Degrees Twaddell.	Degrees Baumé.	Specific Gravity.	Degrees Twaddell.	Degrees Baumé.	Specific Gravity.	Degrees Twaddell	Degrees Baumé.	Specific Gravity.
1	0.7	1.005	64	35.0	1.320	128	56.3	1.640
2	1.4	1.010	66	35.8	1.330	130	56.9	1.650
4	2.7	1.020	68	36.6	1.340	132	57.4	1.660
6	4.1	1.030	70	37.4	1.350	134	57.9	1.670
8	5.4	1.040	72	38.2	1.360	136	58.4	1.680
10	6.7	1.050	74	39.0	1.370	138	58.9	1.690
12	8.0	1.060	76	39.8	1.380	140	59.5	1.700
14	9.4	1.070	78	40.5	1.390	142	59.9	1.710
16	10.6	1.080	80	41.2	1.400	144	60.4	1.720
18	11.9	1.090	82	42.0	1.410	146	60.9	1.730
20	13.0	1.100	84	42.7	1.420	148	61.4	1.740
22	14.2	1.110	86	43.4	1.430	150	61.8	1.750
24	15.4	1.120	88	44.1	1.440	152	62.3	1.760
26	16.5	1.130	90	44.8	1.450	154	62.8	1.770
28	17.7	1.140	92	45.4	1.460	156	63.2	1.780
30	18.8	1.150	94	46.1	1.470	158	63.7	1.790
32	19.8	1.160	96	46.8	1.480	160	64.2	1.800
34	20.9	1.170	98	47.4	1.490	162	64.6	1.810
36	22.0	1.180	100	48.1	1.500	164	65.0	1.820
38	23.0	1.190	102	48.7	1.510	166	65.5	1.830
40	24.0	1.200	104	49.4	1.520	168	65.9	1.840
42	25.0	1.210	106	50.0	1.530	169	66.1	1.845
44	26.0	1.220	108	50.6	1.540	170	66.3	1.850
46	26.9	1.230	110	51.2	1.550	-	67	1.872
48	27.9	1.240	112	51.8	1.560	-	68	1.897
50	28.8	1.250	114	52.4	1.570	-	69	1.921
52	29.7	1.260	116	53.0	1.580	---	70	1.946
54	30.6	1.270	118	53.6	1.590	---	71	1.974
56	31.5	1.280	120	54.1	1.600	---	72	2.000
58	32.4	1.290	122	54.7	1.610	---	73	2.031
60	33.3	1.300	124	55.2	1.620	---	74	2.059
62	34.2	1.310	126	55.8	1.630	---	-	---

NOTE. The degrees in Twaddell's hydrometer bear a direct relationship to the specific gravity and may be obtained from the same by the following formula in which "d" represents the specific gravity and "n" the number of degrees Twaddell. $n = \frac{1000d - 1000}{5}$. On the other hand by the formula $d = \frac{5n + 1000}{1000}$ the degrees Twaddell are

converted into the corresponding specific gravity. For values below 2.0 the degrees Twaddell may be obtained from the specific gravity by moving the decimal point two figures to the right, striking off the first figure and multiplying the rest by 2, as per the following example:

$$\begin{array}{r} \text{Specific gravity} \quad 1.133 \\ 113.3 \\ 113.3 \times 2 \\ \hline 226.6 \text{ Twaddell.} \end{array}$$

TABLE IIB
Output of Principal Products

Kind of goods.	1935		1934.	
	Quantity Th tons.	Value. £'000.	Quantity. Th. tons	Value £'000.
Simple manures :*				
Basic slag	319.9	399	255.5	289
Superphosphates	292.2	733	431.5	1,049
Phosphate rock, ground for sale as such, but not for dissolving	37.7	80	48.0	97
Nitrogenous fertilisers (other than sulphate of ammonia)	90.7	410	79.4	349
Bone meal	27.3	135	76.9	497
Other manufactured fertilisers (guano, fish meal, etc.)	22.2	108		
TOTAL—Simple manures	790.0	1,865	891.3	2,281
Compound manures	508.8	2,856	56.1	470
Disinfectants, insecticides, weed-killers and sheep and cattle dressings, except tobacco offal and nicotine insecticides. } Th galls.	48.6	1,466		54.7
	284	24	397	52
	Th. cwt.		Th. cwt.	
Nicotine, nicotine sulphate, and nicotine insecticides	14.7	106	8.4	74
	Th tons		Th tons	
Glue and size	41.0	924	37.9	832
Gelatine	7.2	577	5.3	458
Bones and horns for manufacturing pur- poses	14.2	84	11.9	71
Bones for manure	6.5	30	—	55
Bones by-products not included elsewhere	--	29		
TOTAL—Principal products	--	7,961	--	6,559

* See introductory note

† This figure relates to compound manures recorded on the basis of the value of the compounding work done, i.e., the selling value of the manures compounded less the value of the fertilisers used as ingredients.

TABLE III
Production, Exports, and Imports

Kind of goods.		Production. Th. tons.	Exports. Th. tons.	Retained imports. Th. tons.
Basic slag	{ 1935	320.0	28.8	8.7
	{ 1934	255.5	36.4	0.6
Superphosphates	{ 1935	447.4	22.7	30.5
	{ 1934	431.5	19.6	49.9
Disinfectants, insecticides, weed-killers and sheep and cattle dressings, except tobacco, offal and nicotine insecticides	{ 1935	49.8*	18.2	0.4
	{ 1934	56.5*	20.3	0.4
		Th. cwt.	Th. cwt.	Th. cwt.
Nicotine, nicotine sulphate and nicotine insecticides	{ 1935	14.7	1.5	0.4
	{ 1934	8.4	0.5	0.7
		Th. tons	Th. tons	Th. tons
Glue and size	{ 1935	41.0	4.1	4.3
	{ 1934	37.9	3.7	3.3
Gelatine	{ 1935	7.2	0.4	2.9
	{ 1934	5.3	0.4	2.6

* Including an estimate of the weight of the output returned in gallons.

The following tables relate only to firms whose returns were made on schedules for the Fertiliser, Disinfectant, Glue and Allied Trades and are summarised in Table I.

TABLE IV

Other Output of the Fertiliser, Disinfectant, Glue, and Allied Trades

The value of the gross output of the firms whose returns were made on schedules for the Fertiliser, Disinfectant, Glue and Allied Trades was £7,416,000 in 1935 and £5,684,000 in 1934, of which £6,500,000 1935 and £4,955,000 in 1934 consisted of products included in Table III. Particulars of the remaining items are shown below.

Kind of output	1935		1934.	
	Quantity Th. tons.	Value. £'000.	Quantity, Th tons	Value. £'000
Sulphate of ammonia	3.1	18	2.2	13
Sulphuric acid (as 100 per cent acid)	18.4	50	17.3	50
Animal oils, fats, and greases:—				
Refined	3.3	66	4.0	67
Not refined	18.1	318	15.3	228
Feeding stuffs, etc., for animals and poultry	26.8	219	21.8	181
Other chemical products	—	72	—	73
Soap, perfumery, etc.	—	75	—	76
Other goods	—	98	—	41
TOTAL	—	916	—	729

TABLE V
Materials, Fuel, and Electricity Purchased and Used

Kind of materials, etc	1935.		1934	
	Quantity. Th. tons.	Cost. £'000	Quantity Th. tons.	Cost £'000.
Phosphate rock (mineral phosphates of lime)	315.4	464	296.5	412
Pyrites	102.4	122	92.9	111
Spent oxide	10.4	9	10.8	9
White arsenic	2.2	30	2.1	31
Cresylic acid	Th. galls. 400	31	Th. galls. 456	33
Carbolic acid crystals	Th. cwt. 0.7	2		
Potash (sulphate, muriate, nitrate, and other potash salts)	1,270.6	309		
Sulphuric acid	Th. galls. 39.0	7		
	Th. tons 37.0	66		
Sulphate of ammonia	72.2	433		
Fuel and electricity used for all purposes	2,406
Coal	190.9	151		
Coke	15.2	11		
Heavy fuel oil	Th. galls. 161	4		
Purchased electricity*	Th. B.T.U. (Kw.hrs) 23.026	69		
All other purchased materials and fuel	—	2,747		
TOTAL	—	4,455	—	3,002

* Including electricity generated in other works under the same ownership.

TABLE VI
Consumption of Electricity in 1935

Electricity consumed	1935 Th B.T.U. (Kw. hrs.).
Generated in same works	8,299
Generated in other works under same ownership	2,394
Purchased	20,632
TOTAL	31,325

TABLE VII

Average Numbers Employed

Persons employed.	Males.		Females.		Total.		
	Under 18.	All ages.	Under 18.	All ages.	Under 18.	All ages.	
Operatives (average for the year):							
1935	362	6,318	290	1,118	652	7,436	
1934	290	5,980	280	1,116	570	7,096	
Administrative, technical, and clerical staff:							
1935	100	1,560	60	596	160	2,156	
1934	106	1,474	54	542	160	2,016	
TOTAL							
	{ 1935	462	7,878	350	1,714	812	9,592
	{ 1934	396	7,454	334	1,658	730	9,112

As at 1935 and 1934.

Figures released by the Commonwealth Statistician show that there are 35 chemical fertiliser factories in Australia (7 in Tasmania, 6 in New South Wales, 6 in Victoria, 6 in South Australia, 5 in Queensland and 5 in Western Australia), employing 2,136 hands. Value of land and buildings is estimated at £1,538,321, and of plant and machinery at £2,295,124. Wages paid during the year amounted to £639,791; value of fuel used was £114,868, and value of materials used, £3,821,267. Total value of output was £5,219,576.¹

¹ *Fertiliser J.*, 24 April, 1946, p. 277.

TABLE 65

International Atomic Weights (1929) and Atomic Numbers

	Atomic number	Atomic weight
Aluminium	13	26.97
Antimony	51	121.76
Argon	18	39.94
Arsenic	33	74.93
Barium	56	137.36
Beryllium	4	9.02
Bismuth	83	209.0
Boron	5	10.83
Bromine	35	79.915
Cadmium	48	112.40
Caesium	55	132.81
Calcium	20	40.09
Carbon	6	12.003
Cerium	58	140.2
Chlorine	17	35.457
Chromium	24	52.04

	Atomic number.	Atomic weight.
Cobalt	27	58.95
Copper	29	63.55
Fluorine	9	19.00
Gallium	31	69.72
Gold	79	197.21
Helium	2	4.002
Hydrogen	1	1.0078
Indium	49	114.8
Iodine	53	126.932
Iridium	77	193.04
Iron	26	55.84
Lead	82	207.22
Lithium	3	6.94
Magnesium	12	24.30
Manganese	25	54.95
Mercury	80	200.60
Molybdenum	42	96.0
Neon	10	20.18
Nickel	28	58.69
Nitrogen	7	14.008
Oxygen	8	16.0
Palladium	46	106.7
Phosphorus	15	30.982
Platinum	78	195.2
Potassium	19	39.105
Rhodium	45	102.9
Selenium	34	79.2
Silicon	14	28.08
Silver	47	107.88
Sodium	11	23.0
Strontium	38	87.63
Sulphur	16	32.065
Tellurium	52	127.5
Thallium	81	204.3
Thorium	90	232.15
Tin	50	118.7
Titanium	22	47.9
Tungsten	76	184.1
Zinc	30	65.38
Zirconium	40	91.2

TABLE 66

Chemical Conversion Factors

Substance.	Formula.	/ by	Gives weight of	Formula.	Remarks.
Ammonia	NH ₃	0.823	Nitrogen	N ₂	---
"	"	3.879	Ammonium sulphate	(NH ₄) ₂ SO ₄	(NH ₄) ₂ SO ₄
"	"	3.142	Ammonium chloride	(NH ₄)Cl	NH ₄ Cl
"	"	3.700	Nitric acid	HNO ₃	---
"	"	4.992	Sodium nitrate	NaNO ₃	---
Nitrogen	N ₂	1.215	Ammonia	NH ₃	---
"	"	4.716	Ammonium sulphate	(NH ₄) ₂ SO ₄	---
"	"	3.820	Ammonium chloride	NH ₄ Cl	---
"	"	4.500	Nitric acid	HNO ₃	---
"	"	6.068	Sodium nitrate	NaNO ₃	---
Phosphoric anhydride	P ₂ O ₅	2.185	Tricalcium phosphate	Ca ₃ (PO ₄) ₂	Ca ₃ (PO ₄) ₂
"	"	1.917	Dicalcium phosphate	Ca ₂ H ₂ (PO ₄) ₂	Reverted or citric-sol. phosphate
"	"	1.648	Monocalcium phosphate	CaH ₁ (PO ₄) ₂	Water-sol. phosphate
Tricalcium phosphate	Ca ₃ (PO ₄) ₂	0.455	Phosphoric anhydride	P ₂ O ₅	---
"	"	0.871	Dicalcium phosphate	Ca ₂ H ₂ (PO ₄) ₂	Reverted or citric-sol. phosphate
"	"	0.749	Monocalcium phosphate	CaH ₁ (PO ₄) ₂	Water-sol. phosphate
"	"	0.539	Lime	CaO	---
Monocalcium phosphate	CaH ₁ (PO ₄) ₂	0.607	Phosphoric anhydride	P ₂ O ₅	---
"	"	1.325	Tricalcium phosphate	Ca ₃ (PO ₄) ₂	---
"	"	1.162	Dicalcium phosphate	Ca ₂ H ₂ (PO ₄) ₂	---
"	"	0.239	Lime	CaO	---
Lime	CaO	1.845	Tricalcium phosphate	Ca ₃ (PO ₄) ₂	---

Substance	Formula.	× by	Gives weight of	Formula	Remarks.
Calcium carbonate	CaCO_3	0.56	Lime	CaO	—
„	„	0.44	Carbon dioxide	CO_2	—
„	„	1.36	Calcium sulphate	CaSO_4	—
Calcium sulphate	CaSO_4	0.412	Lime	CaO	—
Lime	CaO	1.783	Calcium carbonate	CaCO_3	—
„	„	2.426	Calcium sulphate	CaSO_4	—
Potassium oxide or potash	K_2O	1.583	Potassium chloride	KCl	Or muriate of potash
„	„	1.849	Potassium sulphate	K_2SO_4	-
„	„	2.146	Potassium nitrate	KNO_3	-
„	„	1.467	Potassium carbonate	K_2CO_3	—
Potassium sulphate	K_2SO_4	0.54	Potash	K_2O	—
Potassium chloride	KCl	0.631,	„	„	—
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	0.258	Ammonia	NH_3	—
„	„	0.212	Nitrogen	N_2	—

TABLE 67

PERCENTAGE COMPOSITION OF FERTILISER MATERIALS*

The following table of the approximate percentage composition of fertiliser materials is taken from an excellent bulletin just issued by the New Jersey Agricultural Experiment Station.

	Nitrogen (N)	Phosphoric Acid (P_2O_5)	Potash (K_2O)
<i>Nitrogen Carriers</i>			
Nitrate of soda	16.0	—	—
Sulphate of ammonia	20.5	—	—
Nitrate of ammonia	35.0	—	—
Nitrate of lime (calcium nitrate)	15.0	—	—
Nitrate of potash	13.0	—	44.0
Leuna salpeter†	26.0	—	—
Ammo-phos†	10.7	48.0	—
Ammo-phos†	16.5	20.0	—
Leuna-phos†	20.0	20.0	—
Mono-ammonium phosphate	11.0	60.0	—
Di-ammonium phosphate	21.0	53.0	—
Calcium cyanamid	22.0	—	—
Urea	46.0	—	—
Calurea†	34.0	—	—
Calnitro†	{ 16.0 20.5	—	—
Dried Blood	13.0	—	—
Tankage	5.8	12.0	—
Tankage	7.4	10.0	—
Garbage tankage	2.5	5.0	—
Milorganite‡	5.4	3.0	—
Nitroganic‡	5.4	2.4	0.3
Raw bone	4.0	22.0	—
Steamed bone	2.6	24.0	—
King crab	10.0	1.0	—
Dried fish	8.0	8.0	—
Acidulated fish	5.0	3.0	—
Castor pomace	5.0	1.0	1.0
Cottonseed meal	6.6	2.0	1.5
Farm manure	0.5	0.3	0.5
Dry chicken manure	2.1	2.0	1.0
Fresh chicken manure	1.2	0.9	0.5

TABLE 67--continued.

	Nitrogen (N)	Phosphoric Acid (P ₂ O ₅)	Potash (K ₂ O)
<i>Phosphate Carriers</i>			
Rock phosphate	—	28—35	—
Superphosphate	—	16—20	—
Triple superphosphate	—	40—48	—
Basic slag	—	17—18	—
Ammonium phosphate	12	61	—
Potassium phosphate	—	22.7	34.5
Nitrophoska	15	30.0	15.0
Ammo-Phos-Ko	12	24	12
<i>Potash Carriers</i>			
Muriate of potash	—	—	48—50
Sulphate of potash	—	—	48—50
Sulphate of potash-magnesia	—	—	26—28
Manure salts	—	—	20.0
Manure salts	—	—	30.0
Kainit	—	—	12—14
Potassium nitrate	13	—	44.0
Tobacco stems	2.5	—	6.5
Greensand marl	—	1—2	5—7
Wood ashes	—	2	5—6

* The following conversion factors will be found convenient. nitrogen to ammonia, multiply by 1.214; ammonia to nitrogen, multiply by 0.823; tricalcium phosphate to phosphoric acid, multiply by 0.485; phosphoric acid to tricalcium phosphate, multiply by 2.18; phosphoric acid to phosphorus, multiply by 0.437; phosphorus to phosphoric acid, multiply by 2.29; potash to potassium, multiply by 0.83; potassium to potash, multiply by 1.20.

† Trade name for manufactured product.

‡ Trade name for product from sewage disposal plant.

§ Trade name for a manufactured product, the composition of which has varied.

TABLE 68
CHEMICAL ANALYSIS OF VARIOUS FERTILISERS

Fertiliser.	Nitrogen.	Phosphate P_2O_5 .	Potash.
Raw Bones	5.0	22	Nil
Bone Meal	3.5-5.0	20-25	Nil
Steamed Bone Flour	1-2	25-32	Nil
Dissolved Bones	2-3	15-16	
Wood Ashes	—	—	10
<i>Farmyard Manures</i>			
Cow	0.43	0.19	0.44
Bullock	0.62	0.26	0.72
Horse	0.54	0.23	0.54
Liquid	0.20	0.03	0.46
<i>Peruvian Guano</i>			
High Grade	10-14	9-11	2-4
Ordinary Grade	5-8	14-18	2-4
Phosphatic	2.5-3.5	18-32	2-6
Ichaboe Guano	8	9-14	2
Fish Guano	8-10	4.5-9	—
Pure Flesh (fat free)	16.7	—	—
<i>Meat Guano</i>			
High Grade	8-9	4.6-7	—
Phosphatic	4-5	16-18	—
Dried Blood	12	—	—
Hoofs and Horns	12-14	—	—
Hoofs and Horns mixed with bone	10	9-11	
Seaweed (wet)	0.5	0.09	1.8 (75 per cent moisture)
<i>Shoddy</i>			
High Grade	12-14	—	—
Medium	5-8	—	—
Low	3	—	—
Hair	10	—	—
Feathers	9	—	—
Soot, Leather Waste	3.3	—	—

Fertiliser.	Nitrogen.	Phosphate P_2O_5 .	Potash.
<i>Chemical Manures</i>			
Nitrate of Soda	15.5	—	—
Nitrate of Potash	14.0	—	—
Nitrate of Lime	13.0	—	—
Sulphate of Ammonia	20.0	—	—
Nitrolime	15.5	—	—
Superphosphate	—	{ 11.8 13.6 16.0 }	—
Basic Slags : Bessemer	—	20.0	—
Open hearth	—	9.15	—
Sulphate of Potash	—	—	48.5
Muriate of Potash	—	—	45
Kaimit	—	—	12
<i>Human Excreta</i>			
Fæces	1.0	1.1	.25
Urine6	.17	.2

Sewage sludge.	1.	2.	3.	4.
Water	10.1	31.2	40.6	3.55
Organic matter	49.8	24.9	16.8	38.23
Nitrogen	2.32	.94	.55	1.65
P_2O_5	2.27	.80	1.42	1.25
Lime	2.34	24.6	24.45	8.40
Potash	—	Trace	—	—
Insoluble matter	23.27	7.06	5.57	28.28

END

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